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October 20, 2006

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the fourth-quarter FY 2006 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATTreports.html>.

Sincerely,

Venkat Srinivasan
Manager
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	E. Wall	DOE/OFCVT
	K. Abbott	DOE-BSO

LBID-2563 2006_Q4

BATT TASK 1
CELL DEVELOPMENT
TASK STATUS REPORT

PI, INSTITUTION: V. Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE: Cell Development - Cell Fabrication and Testing

SYSTEMS: Graphite/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-energy, high-voltage Li-ion), Graphite/LiFePO₄ (low-cost Li-ion), and Graphite/LiMn₂O₄ (high-power Li-ion)

BARRIERS: Li-ion systems meeting performance, abuse, and life targets.

OBJECTIVES: Establish cell fabrication capability to evaluate BATT-developed, low-cost materials designed for high-power or high-energy.

APPROACH: Test novel materials in standard cells with preset protocols to provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and thereby accelerate the development of EVs, HEVs, and FCEVs. Incorporate novel components developed in the BATT Program into standardized cells, and test using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Optimize electrode configurations based on modeling results (Task 6). Deliver tested cell components to appropriate investigators involved with BATT Program diagnostic projects (Task 5).

STATUS OCT. 1, 2005: The ability to make low-impedance cells repeatably should be in hand. Most materials that go into a battery, *e.g.*, active material and conductive additives, should be characterized with respect to BET, PSA, and SEM analysis. BATT Cell fabrication and test protocol will be released.

EXPECTED STATUS SEPT. 30, 2006: The ability to make cells with minimal introduction of contaminants should be in hand. Initial performance testing of an advanced high energy and an advanced high power system from materials from the BATT Program should be completed.

RELEVANT USABC GOALS: EV: specific energy of 300 Wh/L fully burdened. HEV: power density of 780 W/L fully burdened.

MILESTONES:

- (1) January 2006 – Demonstrate batch-to-batch cell repeatability.
- (2) June 2006 – Develop a test vessel optimized for BATT materials.
- (3) June 2006 – Benchmark an advanced spinel system.
- (4) September 2006 – Benchmark an advanced EV system

PROGRESS TOWARD MILESTONES

(a) Demonstrate batch-to-batch repeatability: **Completed** – see FY06 first quarterly report.

(b) Develop a test vessel optimized for BATT materials – **Completed**: New pouches were acquired based on a lead from a visiting scholar from NEC, a Japanese company working with Nissan to develop a Mn-spinel-based HEV pouch-cell battery. The pouches were tested for leaks by filling them with a gram of electrolyte and aging them at 45°C. Weight measurements were taken every two weeks, which only gives an indication of the difference between electrolyte leaving the pouch and water entering the pouch. None the less, the weight loss for these pouches was approximately 0.12% per month. This was far superior to our previous pouches from Sumitomo Electric Industries (SEI) that showed a weight loss of around 2% per month.

With this change and the repositioning of our cell making equipment into glove boxes, it is anticipated that we will be able to make cells with little water content and test them with little water intrusion. This quarter a coin cell assembly was ordered. Its delivery is contingent on DOE accepting certain use restrictions, which are more targeted for a commercial manufacturer. With arrival of the equipment, it is planned to evaluate the difference between coin cells and pouch cells in the next fiscal year.

(c) Benchmark an advanced spinel system – **Initiated**: As part of the characterization of the Mn-spinel system, the solubility of the spinel in different electrolyte mixtures will be measured. The technique for measuring dissolved manganese was developed this quarter. Oxide is first aged in electrolyte for a month at 55°C. The solution is centrifuged and a sample of liquid extracted. The sample is then digested in nitric acid. This solution is then added to different standard solutions containing manganese, which are also used to calibrate the ICP equipment. The data is then analyzed to determine the Mn concentration in the original sample. It took us several months to find a group willing to let us put our solutions into their ICP and develop a sample preparation technique that did not result in the instrument shutting down. A full evaluation of the Mn dissolution as part of the Mn-spinel benchmarking is intended for the next fiscal year (see AOP for FY2007).

(d) Benchmark an advanced EV system – **Postponed**: The highest energy density system of the BATT baselines is the one based on the 3³rds material. To meet the DOE EV energy targets, it was calculated with the help of Venkat Srinivasan that this cathode will need to be matched with an anode with a capacity of approximately 1000 mAh/g and a voltage around 500 mV above lithium. The re-pursuit of this milestone is contingent upon a leap in alloy-anode development that has yet to be realized in BATT.

Research Beyond the Milestones

Cells of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ of the Gen2 ATD cell design were fabricated and are presently on calendar and cycle life test. LiFePO_4 -based cells received from HQ were put in cold storage for two months. They self discharged. Testing in Swagelok cells of the anode and cathode is presently under way to identify the culprit.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE: Cell Development - Cathode, Anode, and Cell Development

SYSTEMS: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/LiMn₂O₄ (high-voltage, high-power); Gr/LiPF₆+EC:DEC/LiFePO₄ (low-voltage, high-stability)

BARRIERS: Specific energy 150 Wh/kg, energy density 230 Wh/L, 30 ohm-cm² area-specific impedance.

OBJECTIVES: Synthesize and evaluate alternative electrode materials with improved energy density, safety, and stability. Support cell development and diagnostics tasks through chemical and structural characterization of cell components. Investigate mechanisms contributing to impedance rise in composite electrodes.

APPROACH: Identify candidate electrode compositions by systematic comparison of phase diagrams and literature reports. Prepare electrodes with novel materials and/or unique structures for evaluation in small cells. Employ x-ray diffraction (XRD), *in situ* microscopy, vibrational spectroscopies, and electroanalytical techniques to determine the applicability of the new materials to BATT chemistries. Investigate particle isolation mechanisms and their influence on power characteristics of composite electrodes.

STATUS OCT. 1, 2005: Composition and structural analyses of BATT electrodes will have contributed to our understanding of failure and degradation modes in the baseline systems. Overcharge protection for lithium ion cells with cathode potentials above 4.0 V will be achieved using electroactive conducting polymers. Operation of the overcharge protection mechanism at low temperatures and stable performance over 100 cycles will be demonstrated.

EXPECTED STATUS SEPT. 30, 2006: Potentially useful low-cost, high capacity electrode materials will have been prepared and evaluated. A detailed investigation of the mechanism and limitations presented by the LiFePO₄/FePO₄ phase transformation will be completed.

RELEVANT USABC GOALS: Specific energy 150 Wh/kg, energy density 230 Wh/L, 30 ohm-cm² area-specific impedance

MILESTONES: July 2006 – Determine capacity and cycling stability of lithium-magnesium alloy electrodes in liquid electrolyte cells.

PROGRESS TOWARD MILESTONES

Hydrothermal synthesis of LiFePO_4 : Control of particle size and morphology

We continue to study the effects of various synthetic conditions on the morphology and size distribution of crystalline LiFePO_4 prepared by hydrothermal methods. We have found that LiFePO_4 crystals form and grow in aqueous solutions containing lithium, iron (II), phosphate, and sulfate ions through a heterogeneous dissolution and reprecipitation process. Vivianite $[\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ always precipitates first. Within a certain pH range, this phase slowly dissolves, supplying iron and phosphate ions to the growing LiFePO_4 . Reaction parameters including reaction temperature and time, pH of the initial mixture, and overall reactant concentrations are critical. Discrete, well-formed LiFePO_4 crystals with dimensions ranging from 50 nm to tens of microns are synthesized through fine-tuning of these parameters. Smaller crystals are obtained at higher reactant concentrations and a slightly basic pH. These adopt a thin hexagonal plate shape with large ac surfaces (Fig. 1a). The larger crystals obtained in dilute solutions and at lower pH are typically prismatic, with diamond-shaped 010 (ac) faces, and much thicker in the b direction, (Fig. 1b).

Lithium extraction from crystals of different sizes was investigated using chemical oxidation by bromine diluted in acetonitrile. Although crystals with a b -axis thickness $< 2 \mu\text{m}$ were completely converted to FePO_4 by a slight excess of oxidant, thicker crystals were only partially oxidized under the same conditions. For example, the crystals in Fig. 1a, $10 \mu\text{m}$ along b , were only 20% oxidized, even after prolonged exposure to bromine. Optical and electron microscope images indicate that Li has been extracted to a depth of about $1 \mu\text{m}$ from a region parallel to the 010 faces. We propose that as Li is removed at the $\text{LiFePO}_4/\text{FePO}_4$ phase boundary, which proceeds in the a direction across the face of the crystal, there is a limit to the depth from which Li can be removed before the boundary has moved on and left only FePO_4 behind. Once the surface has been converted to FePO_4 , it is no longer possible to establish a phase boundary, and delithiation ceases, because Li cannot pass through the FePO_4 layer.

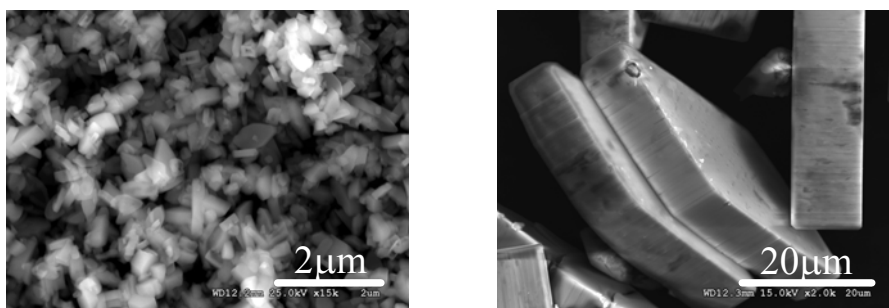


Figure 1. SEM images of hydrothermally synthesized LiFePO_4 crystals

Li-Mg Alloy Anodes: We have shown that dendrite growth is suppressed at Li-Mg alloy anodes. While their capacities are very high, they appear to have limited rate capability ($\sim 0.5 \text{ mA}/\text{cm}^2$) during discharge. A novel method of preparation of Li-Mg cermets containing inert Mg_3N_2 inclusions has been developed and shown to produce electrodes with performance superior to that of the pure alloys. We believe that microporous cermet anodes made by this method may cycle at higher rates due to increased wetted areas.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec (IREQ)

TASK TITLE: Cell Development - Li-ion Polymer Batteries with Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIERS: High costs of Li-ion batteries

OBJECTIVES: Fabricate Li-ion/polymer cells using cell chemistries proposed by DOE and send cells to LBNL for testing. Optimize gel formation as a function of the % plasticizer content, optimize the thermal cross-linked temperature by using a new polymer with different molecular weights (2500, 5000 and 8000). Determine the conductivity of gel electrolytes as a function of plasticizer content, particularly, at low temperature. Study the interface of gel electrolyte in contact with the active electrode materials. Actively collaborate with polymer teams in the BATT Program. Continue developing water-soluble binder (WSB) for use in the anode and cathode. Continue a limited study on ionic liquid systems.

APPROACH: Synthesize and coat electrodes (both anode and cathode) with low-cost materials; evaluate these materials in Li-ion/polymer cells. In addition, focus on gel polymers, as well as studies to identify an appropriate salt and solvent to increase the performance and charge/discharge rate of Li cells at low temperatures. The gel electrolyte will be compared to a liquid electrolyte by measurements in half cells and Li-ion polymer cells at low temperatures.

STATUS OCT. 1, 2005: We will optimize the composition of anode and cathode materials in the electrodes as a function of the WSB (containing no fluoride), with the goal of reducing the amount of binder by 50% compared to standard electrodes with PVDF. To reduce the amount of binder and the cost of the coating, we will demonstrate a new coating process using the WSB in the anode and cathode with focus on LiFePO_4 . Also, we expect to show the effect of the WSB on other baseline chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). Effort will be focused to understand the difference between WSB and PVDF electrodes in term of reversible and irreversible capacity. A limited effort will be focused on the effect of electrode drying; and the influence of temperature, time, and atmosphere in collaboration with LBNL (Kostecki). We expect to evaluate primary cycling data (including the PNGV protocol) from Li-ion/polymer cells containing WSB.

EXPECTED STATUS SEPT. 30, 2006: The cell configuration will be changed from the flat stainless-steel to metal-plastic type. HQ and LBNL teams will collaborate closely to fabricate better cells, beginning with a planned visit by the HQ team to LBNL in September 2005. We expect to show results on the effect of WSB (binder content, slurry viscosity, adhesion) on the cathode and the anode. The reversible and irreversible capacity of electrodes based on WSB will be compared to PVDF electrodes. Our collaboration with LBNL (Kostecki) on diagnostics will provide a better understanding of the effect of WSB and its difference with PVDF. Three different types of polymers, based on polyether as matrix, for gel electrolytes will be studied. Results will be obtained on optimizing gel formation as a function of plasticizer content and the cross-link conditions (temperature and time) after cell sealing. We expect to provide cycling data, including the PNGV protocol, in Li-ion polymer cells that contain gel electrolyte based on polymer-ionic liquid, polymer-liquid electrolyte and 100% liquid electrolyte.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: 1) Dec. 2005, Study the effect of drying temperature in WSB and understand the ICL loss vs. PVDF; 2) Dec. 2005, Deliver LiFePO_4 cells with WSB to LBNL for testing; 3) April 2006, Deliver cells with WSB in both of anode and cathode for testing.

PROGRESS TOWARD MILESTONES

All milestones for FY2006 were completed. We have begun working on the long-term goals of developing the next generation of LiFePO_4 , WSB, and ionic liquids. Our first goal is to optimize the cathode by introducing mixed LiFePO_4 from different synthesis routes. Cathodes based on mixed LiFePO_4 produced by hydrothermal (HD) and solid state (SSR) reactions were coated with carbon. Different (HD)/(SSR) ratios were evaluated, and the optimum performance was found with (HD)/(SSR) = 80/20. The capacity of the cell was 161 mAh/g at C/8. At 10C rate, the cell delivered 104 mAh/g, and at 20C the cell still delivered 49% of the capacity at the C/8 rate.

The second goal is focused on developing a water soluble binder (WSB). A comparative study between PVDF and WSB in the cathode was initiated. The addition of vapor-grown carbon fiber (VGCF) in the cathode greatly improves the performance of the cathode at high rate. In the PVDF-based cathode, the VGCF improved the capacity at 5C to 126 mAh/g from 98 mAh/g for cathode without VGCF. At high rate (12C), the cathode with VGCF delivers 92 mAh/g compared to 49 mAh/g (Fig. 1).

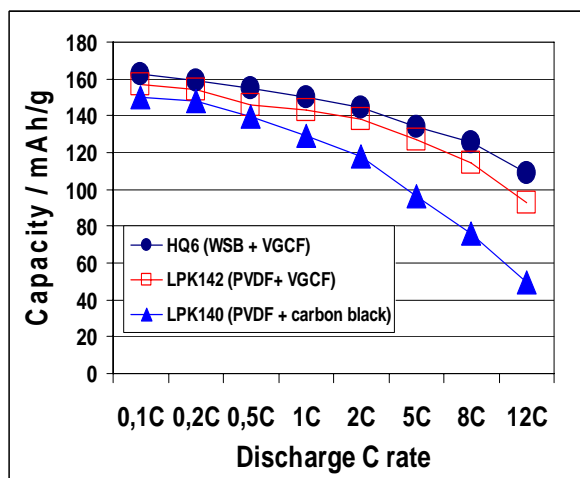


Figure 1: Ragone plot of Li-LiFePO₄ cell in EC/DEC-LiPF₆ with different cathode compositions at 25°C.

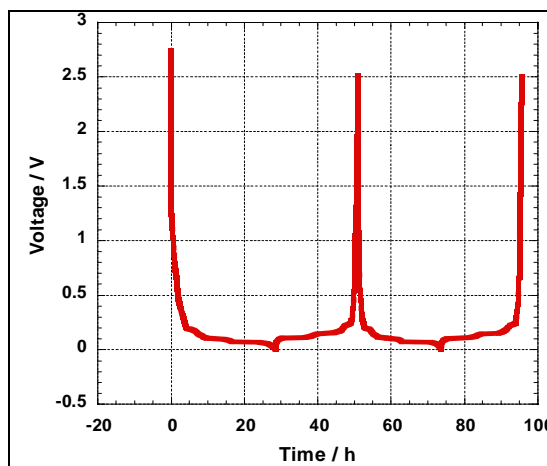


Figure 2: Discharge-charge of coin-type cell: Li/graphite cell with pure ionic liquid + 0.5 M LiFSI at 25°C.

When WSB is used in the cathode instead of PVDF binder, the high-rate performance improved. At 5C, the PVDF-cell delivers 126 mAh/g compared to the WSB-containing cell which yields 133 mAh/g. The cell with WSB showed still better performance when the rate was increased to 12C. The discharge capacity was 15% higher with WSB.

The third goal is focused on studies of the ionic liquid (IL) based bis(fluorosulfonyl)imide (FSI) chemistry in Li cells. We started evaluation of a graphite anode with ILs-FSI and addition of solvent and additives. Figure 2 shows the discharge-charge of Li/graphite using N-méthyl-N-propylpyrrolidinium-FSI + 0.5M Li FSI as electrolyte. This ionic liquid has low viscosity (29 mPa, 20°C) and high conductivity (10.23 mS/cm, 20°C). The coulombic efficiencies for the first and second cycles were 79% and 98%, respectively. The reversible capacity was 342 mAh/g.

The milestone to deliver ten Li-ion cells to LBNL by July 2006 was completed on schedule. Cathodes with WSB based on LTO and LFP films were sent to Clemson University (D. DesMarteau), Brigham Young University (D. Wheeler), and University of Michigan (A.M. Sastry) for analyses.

TASK STATUS REPORT

PI, INSTITUTION: D. Wheeler and J. Harb, Brigham Young University

TASK TITLE: Cell Development - Design, Optimization, and Fabrication of Li-ion Electrodes for High Power Applications

SYSTEM: Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄

BARRIERS: Electrode impedance that limits power density and cycle life

OBJECTIVES: Improve battery power and life through novel electrode structures. Increase understanding of how electrode morphology influences performance. Develop tools to analyze high-rate performance of electrolytes.

APPROACH: We will explore methods for maximizing the high-power performance of low-cost LiFePO₄ composite cathodes. Our efforts will include the use of carbon fibers as conductivity additive in order to improve high-rate performance and diminish capacity fade due to loss of conductivity/connectivity. We will also seek to improve point-to-point electronic connections between the fibers, active material particles, and current collector. In addition, as part of our efforts to optimize ionic conduction, we will conduct Hall-effect experiments and molecular dynamics (MD) simulations in order to determine transport properties for liquid electrolytes.

STATUS OCT. 1, 2005: We will have demonstrated the power improvements possible with carbon fibers added to LiFePO₄ cathodes. Processing steps for the mixing and application of improved cathode slurries will also have been demonstrated. Construction of apparatus for obtaining electrolyte transference number using the Hall Effect will be nearly complete. New intermolecular potentials for MD simulations of the transport properties of LiPF₆ in liquid carbonate electrolytes will be nearly ready for use.

EXPECTED STATUS SEPT. 30, 2006: We will have optimized for the power improvements possible with use of carbon fibers in low-cost LiFePO₄ cathodes, and identified the additional factors that limit performance. We will have shown proof-of-concept results for obtaining the electrolyte transference number using the Hall Effect. MD simulations of the transport properties of LiPF₆ in liquid carbonate electrolytes, as a function of temperature and concentration, will be completed.

RELEVANT USABC GOALS: HEV goals of 30 $\Omega\text{-cm}^2$ ASI, discharge power around 650 W/kg for 10 s, and sufficient cold-cranking power.

MILESTONES:

- (1) January 2006 – Demonstrate that Hall Effect can be used to reliably measure electrolyte transference numbers.
- (2) May 2006 – Optimization of LiFePO₄ cathode by varying active-material loading, carbon-fiber length, and amount of conductivity additive.

PROGRESS TOWARD MILESTONES

Our primary tasks are to fabricate and test cells in order to determine morphologies and material combinations that enable high-rate HEV performance for LiFePO_4 cathodes, and to better understand the associated physical processes. As described more fully below, during the fourth quarter of FY 2006 we continued cycle-life testing of cells. Additionally we began building an improved computer model of the rate-limiting processes in composite electrodes.

Figure 1 shows HEV cycle-life data (still ongoing) for three different LiFePO_4 cells constructed with active material obtained from Hydro-Québec. The curves are largely flat, showing good HEV-cycle performance.

Following the BATT review meeting, we spent significant time this summer to diagnose and remedy possible problems with our cell construction and testing. We identified a few problems that have now been remedied, including retiring a battery tester that was not functioning properly.

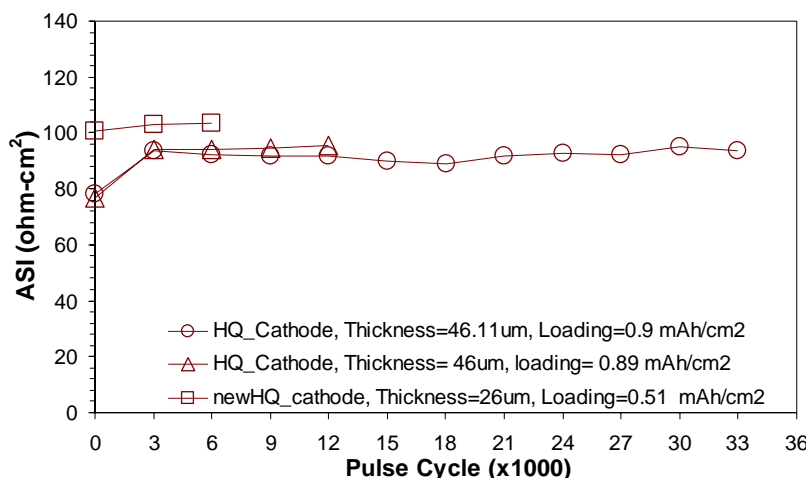


Figure 1. HEV cycle-life testing of area-specific impedance for recently constructed cells. The anodes are lithium metal. Each pulse cycle consists of 10-s discharge, 40-s rest, 10-s charge, and 40-s rest. Pulses were performed at the 5C rate and at 30% DOD. The ordinate is the ASI for a discharge pulse instead measured at 50% DOD every 3k cycles, according to BATT protocol.

Phase-change behavior has been incorporated into our Li-ion battery model in order to better describe LiFePO_4 as an active material. Also, we began investigating mass-transport limitations in the liquid phase that, based on experimental evidence, appear to contribute significantly to the low performance of cells at high rates. In the next quarter we will incorporate this physical phenomenon into our model and validate the model using experimental results. This advance in state-of-the-art battery modeling will allow us to better determine schemes to mitigate this poor performance.

BATT TASK 2

ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Anode Materials

SYSTEMS: Graphite/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂; Graphite/LiBOB+γBL:EA/LiMn₂O₄

BARRIER: Cost, low temperature- and abuse tolerance limitations of Li-ion batteries

OBJECTIVES: To replace graphite with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project addresses the need to improve the capacity, rate capability and irreversible capacity losses of intermetallic electrodes as well as the low temperature operation and abuse tolerance of Li-ion cells.

APPROACH: Our approach over the past few years has been to search for inexpensive intermetallic electrodes (powder laminates rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of at least 300 mAh/g (>1000 mAh/ml). We are focusing predominantly on Sn-based systems that appear to have a good chance of success in practical cells (cf. Sony 'Nexelion' cells). We will continue to study Sb and Si systems as these systems provide valuable information about reaction mechanisms and first-cycle irreversible capacity loss. We will continue our studies of FMC Corporation's stabilized lithium metal powder product (Lectro™ Max Powder) in an attempt to eliminate first-cycle irreversible capacity loss. Promising electrodes will be evaluated in full cells against the high capacity metal oxides of our cathode project (Task 4.1).

STATUS OCT. 1, 2005: Studies of Lectro™ Max powder (formally called SLMP) were initiated. Tentative conclusions from the studies were: 1) Lectro™ Max reacts more readily with insertion compounds (*e.g.*, graphite and Li₄Ti₅O₁₂) than with those that operate by displacement reactions (Cu₆Sn₅, Cu₂Sb, SnO), and 2) that Lectro™ Max was more effective in countering the first-cycle capacity loss of graphite electrodes than intermetallic electrodes (*e.g.*, Cu₂Sb) and metal oxide electrodes (*e.g.*, SnO_x). Rate studies showed that Cu₆Sn₅ performs better than Cu₂Sb at room temperature and at 0°C.

EXPECTED STATUS SEPT. 30, 2006: Progress will have been made in reducing the first-cycle capacity loss of Sn-based intermetallic electrodes with Lectro™ Max; capacity retention on cycling will have been improved and the performance of the intermetallic electrodes against the metal oxides of Task 4.1 in full cells determined. A comparison of the low temperature behavior and rate capability of intermetallic electrodes *vs.* graphite electrodes will have been made.

RELEVANT USABC GOALS: 10 year life, <20% fade over a 10-year period.

MILESTONES:

- (1) September 2006 – Achieve less than 10% first-cycle capacity loss of Sn-based intermetallic electrodes and >300 mAh/g for more than 100 cycles. Determine low temperature capability
- (2) September 2006 – Evaluate performance of intermetallic/lithium metal oxide

PROGRESS TOWARD MILESTONES

Accomplishments

We have initiated studies to develop methods to prepare nanosized intermetallic electrode particles for use in Li-ion cells. Our recent work has focused predominantly on synthesizing materials using high energy ball milling (HEBM) of metal elements, direct synthesis at elevated temperature with subsequent mechanical particle size reduction, and a molten spray pyrolysis method. With Sony's decision to use CoSn as the anode for its 'Nexelion' battery, there has been a renewed interest in this class of Sn-based intermetallic materials. At the last BATT review (June, 2006) it was reported that the intermetallic particles in the 'Nexelion' anode were 5-10 nm in size and approximately spherical in shape. These features seem to indicate a solution-based synthesis method. We are, therefore, reinvestigating such techniques to prepare intermetallic materials.

A solution method that we employed several years ago was based on the zinc reduction of metal salts dissolved in organic solvents at elevated temperatures, *e.g.*, 200°C, with subsequent annealing. For the Cu-Sn system, typical products included the desired product Cu_6Sn_5 , as well as $\text{Cu}_{41}\text{Sn}_{11}$ and metal oxide impurities. Using this technique, the Cu_6Sn_5 particles prior to annealing exhibited a dendritic morphology (Fig. 1a); these materials did not provide satisfactory electrochemical properties exhibiting fade on cycling possibly due to loss of active material.

Building on this work, we are now exploring the use of various alternative reductants in organic solvents in an attempt to synthesize compositionally homogenous intermetallic materials. Attempts to use common alcohols, such as ethanol and isopropanol, although leading to increased metal salt solubility also tended to yield more metal oxide by-products. Efforts to use potassium borohydride (KBH_4) instead of zinc have been more successful, which we attribute to the solubility of KBH_4 in the host solvent, although notably with alcohols there was evidence of solvent reactivity. Our best results, to date, have been obtained using the high boiling point solvent tetraethylene glycol (TEG) as it dissolved adequate amounts of the metal salts and was stable to KBH_4 . For the Cu-Sn system, a stoichiometric mixture of salts was added to the solvent system and reduced to form suspended copper and tin particles. Heating the sample to 130°C resulted in near single phase Cu_6Sn_5 . SEM images of the as-prepared materials revealed 100-200 nm primary particles, agglomerated into larger 2-5 μm grains, in contrast to 0.5-35 μm sized primary particles obtained by HEBM and 10-20 μm by spray pyrolysis; using this method, the Cu_6Sn_5 particle morphology after annealing was similar to that obtained from melts (Fig. 1b).

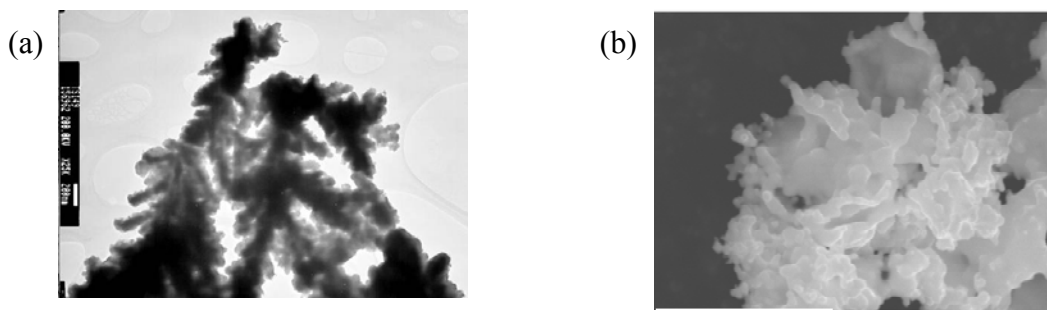


Figure 1. SEM's of (a) dendritic Cu_6Sn_5 isolated using a Zn reductant, and (b) Cu_6Sn_5 using a KBH_4 reductant, annealed at 130 °C.

Future work will focus on extending this methodology to other binary and ternary intermetallic compounds, notably those containing cobalt and tin, and on the electrochemical characterization of these materials.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE: Anodes - Novel Materials

SYSTEMS: Li-Ion: all systems.

BARRIER: Cost, safety and volumetric capacity limitations of lithium-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with low cost manganese oxide and phosphate cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure lithium (to minimize risk of lithium plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2005: We have shown that bulk vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure aluminum foil, expanded metal and aluminum alloys were found to have a high capacity, react readily with lithium but their capacity faded rapidly on cycling in carbonate-based electrolytes. Tin containing materials such as MnSn_2 cycle well for a few cycles before capacity fade sets in. Pure tin foil anodes of grain size below a micron cycle better, but the cell impedance was found to increase markedly after about ten cycles.

EXPECTED STATUS SEPT. 30, 2006: From our program to understand capacity fade of tin on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, to have studied electrical connectivity by using a reactive support, and to have improved the electrochemical performance of the materials identified. Specifically we will know how the surface of tin changes on cycling, and what impact the depth of discharge has on capacity retention. We will also have begun to have an understanding of whether going nano will help solve the anode issues or exacerbate them.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

MILESTONES:

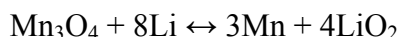
- (1) July 2006 – Identify the surface changes on tin foil during cycling and as a function of the electrolyte working collaboratively with LBNL.
- (2) August 2006 – Define the key parameters determining capacity fade in pure tin and its alloys, and determine and understand impact of depth of cycling on capacity fade (HEV vs. EV).

PROGRESS TOWARD MILESTONES

In the prior quarters we reported on the electrochemistry of tin based anodes, showing that although they had higher initial capacities than carbon-based anodes the capacity rapidly decays after 10 to 15 cycles to values comparable to that of graphite. We also showed that amorphous nano-size tin cobalt materials have excellent reversibility and comparable gravimetric capacity to that of graphite, but they appear to require the expensive cobalt as a prime component.

This quarter we report on the oxide based materials as anode. Although a number of studies have focused on transition metal oxide such as cobalt oxide CoO or Co₃O₄, manganese oxides have been notable for their absence. Our strategy was to form nanosize particles of the oxide in the hope that they would not decrepitate on reaction during the cycling process. To give these particles some strength we also chose to use fibers, which would form an interwoven mat. We therefore made the desired manganese oxide nanofibers by using a polymer-templated electrospinning process followed by heat treatment to remove the polymer. This resulted in 200-300 nm diameter oxide fibers, and these were found to be electrochemically active. The major phase present is Mn₃O₄.

The electrochemical behavior of these manganese oxide nanofibers is shown in Fig. 1, for discharge/charge cycles at 0.5mA/cm². The discharge and charge curves indicate a single-phase reaction. We believe the reversible reaction of transition metal oxide with Li is:



This large Li insertion leads to a high theoretical capacity of over 900 mAh/g. After the first cycle the capacity decays steadily reaching a plateau between 400 and 500 mAh/g by the 50th cycle. The absence of a catastrophic capacity loss after a few cycles as observed for tin foil signals that electrospun oxides have promise for anodic use in lithium batteries, and maybe even for cathodes. We are now exploring why there is a fade, and trying to understand a larger than theoretical Li insertion capacity in the first cycle.

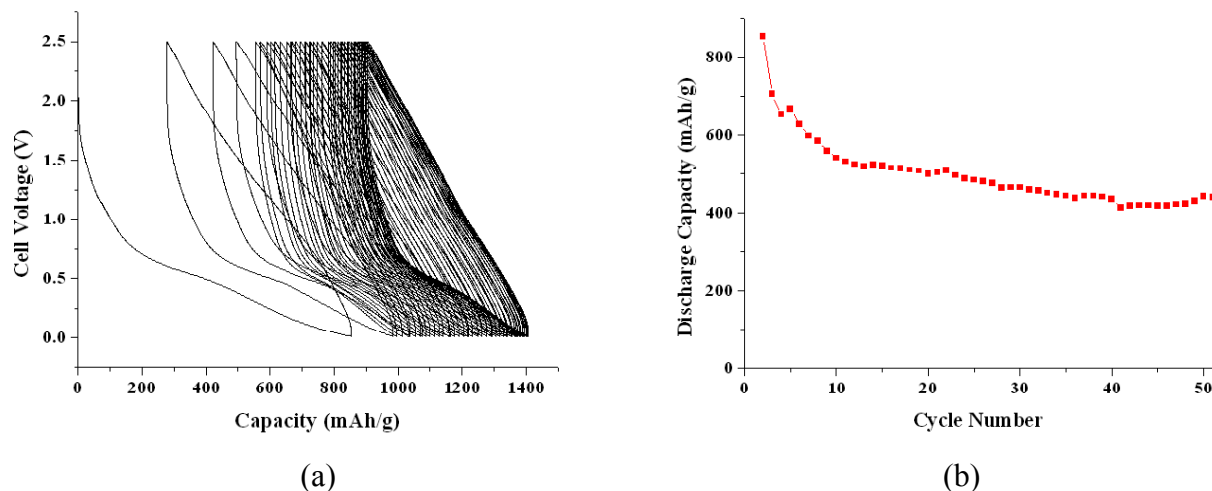


Figure 1. Electrochemical behavior of electrospun manganese oxide showing (a) the smooth cycle profiles suggesting single phase type behavior and (b) the capacity retention on cycling.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

TASK STATUS REPORT

PI, INSTITUTION: A. West, Columbia University

TASK TITLE – PROJECT: Anodes - An Investigation of the Stability of the Lithium Metal Interface

SYSTEMS: Li/Polymer/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

BARRIERS: Interfacial instability (dendrite formation) during charge of Li metal anodes leads to limited cycle life

OBJECTIVES: Understand the influence of electrolyte composition, deposition rate, and applied potential on interfacial stability of Li in liquid and polymer electrolytes. Investigate the root causes (mechanisms) of dendrite formation.

APPROACH: Dendrite formation and growth will be monitored by electrochemical and optical methods as a function of electrolyte composition and applied potential. In an attempt to study the cause or causes of dendrite formation, the impact of pulse plating parameters on dendrite formation will be considered. Furthermore nucleation and growth of Li deposits will be characterized by electrochemical methods.

STATUS OCT. 1, 2005: Glove box and other laboratory equipment will be purchased and assembled.

EXPECTED STATUS SEPT. 30, 2006: An investigation of the impact of deposition conditions on dendrite formation and growth in select liquid electrolytes will be completed. Methodologies for characterization of dendrite formation will have been evaluated. Plans to transition the work to include polymer electrolytes and to test theoretical stability models will be on-going.

RELEVANT USABC GOALS: Specific Energy = 200 Wh/kg and Specific Power = 400 W/kg; Energy Density= 300 Wh/l and Specific Power= 600 Wh/l; 1000 cycles

MILESTONES:

- (1) March 2006 – Establish Columbia University experimental setup and evaluate methods of characterizing dendrite formation.
- (2) September 2006 – Quantify the influence of electrolyte properties and deposition conditions on dendrite formation and growth.

PROGRESS TOWARD MILESTONES

This project is an attempt to understand the mechanism of dendrite formation during charging of a secondary Li battery. The mechanism for dendrite formation during the deposition of other metals (*e.g.*, copper) is well understood, dendrites propagate rapidly as the deposition current approaches the limiting current. However, dendrites form at currents well below the limiting current during Li deposition, and the exact mechanism is unclear.

Early experimental attempts to quantify Li dendrite growth turned out to give unreliable data. Li was deposited onto Cu or Ni from a LiPF_6 in PC:DMC electrolyte bath. The Li substrate was then rinsed with pure DMC and allowed to dry. *Ex situ* surface profiles were then measured to determine the surface roughness. However, the surface roughness increased with increasing air exposure time. This showed us we needed to use an *in situ* method that avoids errors related to the plated Li reacting with atmospheric oxygen and humidity to measure dendrite growth.

We have started to install an *in situ* optical microscopy station inside our existing glove box. A Carl Zeiss Stemi 2000-C stereomicroscope with upgraded eye pieces and lens that will allow for 250x magnification over a 1 mm^2 field of view, which according to literature [*Journal of Power Sources* 81–82 1999, 925–929] should allow us to view dendritic growth, was moved into the glove box. Also an Edgetech Dew 1-C trace moisture analyzer (<1 ppm water sensitivity) has been added to ensure the water does not have an adverse effect on any of our results. An additional Swagelok cell to increase our current experimental capacity and syringe pumps to introduce electrolytes to microfluidic test cells (described below) have also been installed in the glove box.

We also have been building microfluidic test cells to get a clear, reproducible view of the electrode/electrolyte interface. The cell consists of two similar PDMS molds into which working, counter, and reference electrodes are inserted (shown below). In between the electrodes, there is an electrode/electrolyte interface area (area A) that is connected to a reference electrode and an electrolyte reservoir (area B) to prevent electrolyte depletion and minimize any effect of the counter electrode. The flow channels are approximately $150\text{ }\mu\text{m}$ in height. The cell will give us a working electrode area of approximately 0.15 mm^2 . Preliminary tests are now being performed of Cu deposition at high percentages of the limiting current to attempt to observe Cu dendrite growth. Additional tests also have shown that LiPF_6 electrolyte is compatible with the materials (mainly PDMS) used to fabricate the microfluidic cell.

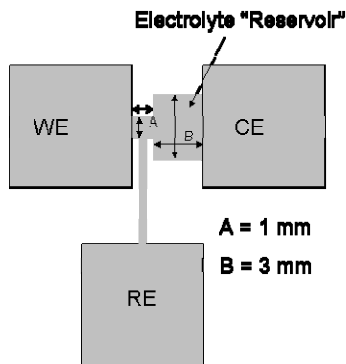


Figure 1. Sample microfluidic cell used to view dendrite growth.

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N.P. Balsara, Lawrence Berkeley National Laboratory

TASK TITLE: Electrolytes - Development of Polymer Electrolytes for Advanced Lithium Batteries

SYSTEMS: Li/polymer/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

BARRIERS: Dendrite formation in Li-metal batteries leading to short lifetimes.

OBJECTIVES: Study the stability of PS-PEO electrolytes against Li electrodes. Synthesize PS-PEO diblock copolymers to obtain electrolytes with high ionic conductivity and shear modulus. Establish a laboratory dedicated for sample preparation and physical characterization of dry polymer electrolytes

APPROACH: Synthesize and characterize robust nanostructured dry polymer electrolytes with high conductivity and high shear modulus that resist dendrite growth during cell cycling. Synthesize polymer and characterize salt/polymer mixtures using AC impedance spectroscopy. Test promising candidates for stability against Li electrodes and in Li cells in collaboration with members of the BATT Program. Fully characterize the materials of interest using additional methods such as neutron and light scattering, rheology, and transmission electron microscopy.

STATUS OCT. 1, 2005: A series of polystyrene-polyethyleneoxide (PS-PEO) block copolymers have been synthesized. Mechanical and electrical properties of a 60 kg/mol, 0.38 volume fraction PS-PEO copolymer with added Li[N(SO₂CF₃)₂] will be measured using rheology and AC impedance spectroscopy. The morphology of the systems will be fully characterized by X-ray scattering and electron microscopy.

EXPECTED STATUS SEPT. 30, 2006: Continued characterization of nanostructured PS-PEO electrolytes including stability tests against Li electrodes and cell testing. Better understanding of polymer structure using microscopy and scattering. Examine dependence of parameters such as molecular weight, volume fraction, sample thickness, and rheological properties on behavior of solid polymer electrolyte. Build a new laboratory at Lawrence Berkeley National Lab for physical characterization and preparation of dry polymer electrolytes. Equipment will be a top-of-the-line glovebox containing an automated sample press, a rheometer, AC impedance measurement, and a Li electrode deposition system.

RELEVANT USABC GOALS: Specific Energy = 200 Wh/kg and Specific Power = 400 W/kg; Energy Density= 300 Wh/l and Specific Power= 600 Wh/l; 1000 cycles

MILESTONES:

- (1) February 2006 – Determine stability of current dry polymer electrolyte against Li electrodes.
- (2) September 2006 – Characterize new dry electrolytes.

PROGRESS TOWARD MILESTONES

In the last quarter we had begun a systematic study of ionic conductivities for a variety of poly(styrene-*block*-ethyleneoxide (SEO) copolymers with LiTFSI salt. Measurements were made as a function of salt concentration, temperature, and molecular architecture of the copolymer. At a fixed salt concentration (r =molar ratio of Li to ethylene oxide=0.02), we saw a monotonic increase in conductivity with increasing molecular weight of the copolymer. We thus focused on the polymer with the highest molecular weight. Figure 1 shows results obtained with the r =0.085 which is the highest conductivity that we have recorded thus far. Obtaining conductivities as high as 10^{-3} S/cm in a copolymer where the major component is non-conducting is, to our knowledge, unprecedented.

The interface between Li metal and our polymer electrolytes was studied by constructing Li/polymer/Li cells. The Li metal was evaporated onto the electrolyte in a vacuum chamber. Preliminary results of reversing a DC current of $76 \mu\text{A}/\text{cm}^2$ through a copolymer electrolyte with r =0.02 (1/2 the estimated limiting current density for our system) are shown in the voltage versus time plot in Fig. 2. The lack of change in the cycling data indicates stability of the polymer/Li interface.

We have thus completed the two milestones given above.

Further Plans to Meet or Exceed Milestones:

We will continue to study the conductivity of SEO salt mixtures and the stability of the Li/polymer interface. Progress during the next quarter will be slow as new students will have to learn how to synthesize polymers, and make conductivity measurements. Toward the end of the quarter, we will begin the assembly of full cells that will directly address the milestones.

Reason for Changes in Milestones: None

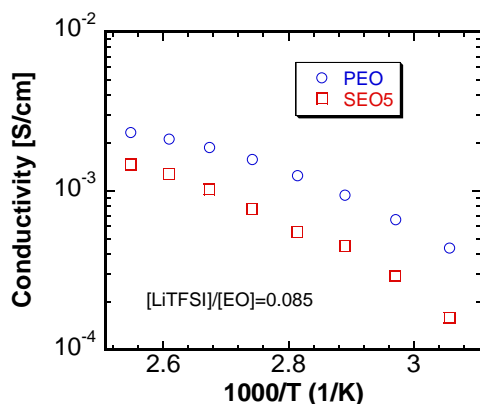


Figure 1. Conductivity of the copolymer as a function of temperature compared to a pure PEO homopolymer.

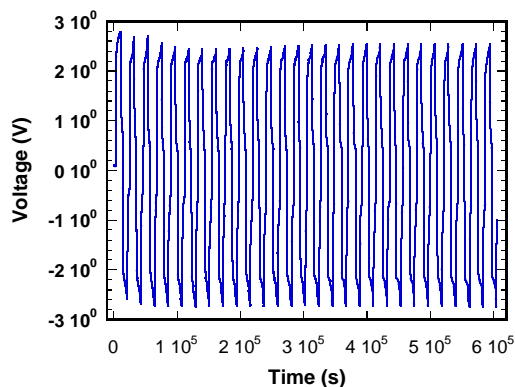


Figure 2. Results of cycling experiments on Li/polymer/Li cells.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/LiMn₂O₄ (high-voltage, high-power); Gr/LiPF₆+EC:DEC/LiFePO₄ (low-voltage, high-stability)

BARRIERS: Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade, low abuse tolerance.

OBJECTIVES: Determine and quantify the improvement (if any) in abuse tolerance of polymer gel electrolytes over liquid electrolytes. Determine the limitations on Li-ion transport in polymer gel electrolytes and the electrolyte component of composite electrodes and develop materials capable of high power operation at ambient temperature with lithiated carbons/Li metal alloy anodes and high voltage cathode materials. Determine the feasibility of the use of Li metal and lithium alloy electrodes with polymer gel electrolytes and provide operating conditions that prevent dendrite growth and provide high coulombic efficiencies (>99.9%) at HEV rates as well as under EV cycling conditions.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2005: The effects of gels on abuse tolerance and transport properties will be determined. The transport performance of single-ion conductor gels will be compared with the binary systems. Compatibility of the polymer electrolyte and polyelectrolyte gels with lithium metal, graphite electrodes and composite cathodes will have been explored, with particular reference to the interfacial impedance.

EXPECTED STATUS SEPT. 30, 2006: The effects of impurities such as water on the impedance behavior of liquid and polymer gel cells will be determined for both calendar and cycle life cells. The effects of polymer gels on the impedance behavior of base line cells will be ascertained for gels that do not penetrate the composite electrodes. Exploratory experiments will be carried out for lithium alloy anodes with elastic binders.

RELEVANT USABC GOALS: 15 year life, <23% power fade, 30 ohm-cm² area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge, short circuit and high temperatures (>60°).

MILESTONES:

- (1) September 2006 – Quantify the effect of impurities such as water on interfacial properties for liquid and gel electrolytes.
- (2) September 2006 – Quantify the effect of gel polymer electrolytes on interfacial properties relative to liquid electrolytes.

PROGRESS TOWARD MILESTONES

1. Abuse Tolerance of Electrolytes. TGA measurements of gel polymer electrolytes (EC/EMC-LiPF₆ with cross-linked polyethers (PEO-type) and PVDF (phase separating) shows that the presence of the polymer does little, if anything, to suppress the volatility of the liquid electrolyte components. Thus flammable vapors are produced even at room temperature resulting in a safety issue if the cell is breached. Polymer gels prepared with typical Li-ion battery electrolytes therefore offer no significant safety improvement over liquid electrolytes. By contrast, ionic liquid gels prepared using pyrrolidinium TFSI salts are completely stable to 200°C and it is the polymer that generates the volatile vapors not the electrolyte. Ionic liquid electrolytes therefore show significantly better thermal behavior. This also includes stability towards reaction with nascent oxygen evolving from decomposing cathode materials. DSC measurements show reaction of Gen-2 and 1/3,1/3,1/3 cathodes with EC/EMC-LiPF₆ electrolytes at around 150°C whereas ionic liquid electrolytes do not react until temperatures of 300°C are reached.

Chemical reactivity experiments with EC/EMC electrolyte components show that PF₅ reacts at sub-zero temperatures to initiate polymerization reactions. PF₅ reacts more rapidly in a sealed reaction flask with polyethers than with the carbonate solvents to form fluorophosphates and phosphate anions. This then solves the riddle of what the polymerization reaction produces. When LiF is added to the solvent components it completely suppresses these reactions by preferentially reacting with the PF₅. LiF appears to be soluble in EC/EMC up to at least 1 molal. This property suggests a method to produce very pure electrolytes by reaction of pure gaseous PF₅ with thoroughly dried and purified EC/EMC-LiF solution. This electrolyte contains no protic species and cannot form HF.

2. Effects of impurities, particularly water, on interfacial behavior of electrolytes. Karl-Fischer(K-F) titration and potentiometric measurements of electrolytes have been developed to provide quality control methods for electrolytes. We have confirmed the measurements made by A. Weber of Energizer that any water present in the original solvent is converted to HF over time. Thus K-F titration is insufficient for quality control of electrolytes and a measure of the HF must be included. Thus all sources of water in a cell must be accounted for as they produce HF. The HF initiates polymerization reactions of the electrolyte and produces side reactions during cell formation and cycling. These polymerization reactions are suppressed if the electrolyte is kept sealed in a container where CO₂ cannot be removed.

The products resulting from the impurities appear to correlate with the interfacial impedance measured at the electrodes. With Li metal a stable SEI does not appear to form with EC-EMC-LiPF₆ electrolytes and a large initial impedance continues to grow with time. On graphite anodes the initial impedance is much smaller due to the lower reactivity of the graphite anode. However, the rate of growth of the impedance at the graphite anode is a complex process that is dependent upon the concentration of the impurities and how the original formation process is carried out. We intend to provide a better quantitative relationship with a more complete analytical measurement of the chemistry in conjunction with the cell cycling.

We note that the presence of polyether polymer gels produces considerably larger impedances at anodes than liquid electrolytes.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan and P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE: Electrolytes - Composite Polymer/Gel Electrolytes for Lithium and Lithium-ion Batteries

SYSTEMS: Low Cost Electrolytes for lithium-ion and lithium systems

BARRIERS: Short lithium battery lifetimes, poor polymer transport properties, and high costs

OBJECTIVES: Develop composite polymer/gel electrolytes that are low cost, mechanically strong, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long-cycle life.

APPROACH: Use surface-functionalized fumed silica fillers in BATT-baseline systems (lithium-ion batteries for HEV) to determine the effects of filler type and concentration on interfacial stability and cell capacity upon cycling. Fumed silica-based polymer gel electrolytes are also examined for possible utility in rechargeable lithium systems (EV application). We attempt to correlate these electrochemical characteristics with mechanical properties and materials chemistry (e.g., silica-type, salt, or PEO-type, with novel materials supplied by G. Baker, D. DesMarteau, or J. Kerr). Data collected include modulus, ionic conductivity, interfacial resistance, lithium cycling efficiency, and full-cell cycling capacity.

STATUS OCT. 1, 2005: The effects of adding fumed silica into low-molecular weight (MW) polymer on the charge-discharge cycle performance, electrochemical efficiency, rate capabilities, and self-discharge performance of Li/V₆O₁₃ cells have been completed. Rheological properties, conductivity, and interfacial stability of fumed silica-based electrolytes of high-MW polymer and mixed-MW (low- + high-MW) polymer gel have been investigated. The variation of mass ratio of low- to high-MW polymer in blends of fumed silica-based composite electrolytes reveals a maximum in elastic modulus and yield stress. Dendrite-inhibition effect by fumed silica in low-MW and mixed-MW PEO solvents have been demonstrated by electrochemical and in-situ microscopy. The attenuation effect of aluminum corrosion by fumed silica has been demonstrated. Single-ion conducting fumed silica (R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate, R711-pLiAMPS) has been synthesized with a maximum lithium transference number 0.78. The electrochemical studies show that 1M LiBETI/EC:PC:DEC:DMC (1:1:1:1) + 10%R805 gel electrolyte is a promising electrolyte candidate for lithium-ion batteries used in hybrid electric vehicles.

EXPECTED STATUS APRIL 30, 2006: We will study LiBOB (lithium bis(oxalato)borate) salt-based liquid electrolyte using γ -butyrolactone (GBL) + ethyl acetate (EA) + ethylene carbonate (EC) as cosolvents. We will expand the scope of our work to explore effects of adding fumed silica into the above electrolytes for lithium-ion systems including rheological and transport properties. We will write a final report.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (1) April 2006 – Investigate the effects of salt amounts, solvent compositions, and silica amounts and types of LiBOB/GBL+EA+EC liquid electrolytes on transport and rheological properties. (2) April 2006 – Complete a final report.

PROGRESS TOWARD MILESTONES: Working on final report

TASK STATUS REPORT

PI, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE: Electrolytes - New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

SYSTEMS: Graphite/LiFePO₄ (Low-voltage, high-stability)

BARRIERS: Poor electrolyte transport, low power, short life, abuse tolerance.

OBJECTIVES: (1) Continue synthesizing ionic-melt electrolytes with low-lattice-energy anions attached to suitable a plasticizer, scaffold or solvating matrix (*e.g.*, polyether oligomer); (2) Characterize the resulting electrolytes with respect to structure, transport properties, reactivity, and especially charge-discharge behavior in Graphite / electrolyte / LiFePO₄ cells.

APPROACH: Salts will be synthesized using variants of methods developed at Clemson over the last 20 years, with recent focus on attachment of fluorosulfonate and fluorosulfonimide anions onto polyether alkoxides. Transport properties will be measured using impedance combined with potentiostatic and galvanostatic polarization and restricted diffusion techniques. Half-cell and full-cell cycle testing will be performed in-house at Clemson on small (*e.g.*, Swagelok) cells in collaboration with BATT coworkers who will provide materials (laminated electrodes) and help with transfer of test protocol knowledge.

STATUS OCT. 1, 2005: Plasticized ionic melt electrolytes of general structure (X)-O-CF₂CHFO-CF₂CF₂-salt where salt = SO₃Li or SO₂N(Li)SO₂CF₃ and X = polyether will have been synthesized and characterized with respect to structure, purity, and ionic conductivity. Preliminary cell testing in collaboration with BATT coworkers at NCSU will have been completed. Reactivity / abuse testing is on hold pending cell testing which will provide materials from disassembly of charged cells for thermogravimetric and calorimetric analysis.

EXPECTED STATUS SEPT. 30, 2006: In-house testing of small cells made using ionic melt electrolytes and tested under various charge/discharge rates and conditions will be complete. Reactivity testing on materials from disassembled charged cells will be complete. A new generation of ionic melt electrolytes of general structure [polyether-OC₆H₄-salt] where salt = -SO₃(Li) or -SO₂N(Li)SO₂Rf, and composite electrolytes comprised of solid-state Li ion conductors dispersed in ionic melts, will be synthesized and characterized.

RELEVANT USABC GOALS: 15 year life, <23% power fade, specific power 625 W/kg at the system level.

MILESTONES:

(1) May 2006 - Develop in-house cell testing capabilities for small (Swagelok) cells and use those capabilities to do variable-rate charge-discharge cell testing of Graphite/electrolyte/ LiFePO₄ cells with ionic melt electrolytes already in hand.

(2) September 2006 - Synthesize and characterize new ionic melts of general structure [polyether-OC₆H₄-salt] where salt = SO₃(Li) or SO₂N(Li)SO₂Rf with Rf = CF₃ or C₄F₉.

PROGRESS TOWARD MILESTONES

Most work in the reporting period continued to be focused on ionic melt electrolytes of structure (X)-O-CF₂CHFO-CF₂CF₂-salt where salt = SO₃Li or SO₂N(Li)SO₂CF₃ and X = polyether. Of particular interest is electrolyte IM550, for which salt = SO₂N(Li)SO₂CF₃ and X = polyethylene glycol (PEG) monomethyl ether of MW 550 Da. We studied concentration polarization in IM550 using galvanostatic DC polarization techniques at variable applied current in cells having IM550 electrolyte interposed between dual lithium titanate electrodes. Applied potentials needed to achieve setpoint currents were found to be invariant with time for several hours following application of the current, which would not be the case if salt concentration polarization was occurring. Similar experiments using LiTFSI dissolved in a PEG solvent showed gradual increases in applied voltage with time that were larger when the applied current was larger, as expected if salt concentration polarization was occurring. These data provide further evidence for a lack of salt concentration polarization when current is passed through the IM550 electrolyte.

Rheological studies on IM550 samples in the presence and absence of added PEG plasticizer were performed. Results from dynamic cone-and-plate rheology measurements on IM550 alone at ambient temperature are shown in Fig. 1. The near-zero value for the elastic modulus over the full frequency range confirms the viscous liquid character of the IM550 electrolyte. Steady-state viscosity measurements of PEG-plasticized IM550 samples revealed a strong plasticization effect of the PEG. At ambient temperature and 1.0 s⁻¹ rotation rate, the viscosity decreased from 117 Pa s without plasticizer to 4.8 Pa s with 20 percent plasticizer added. Even larger effects were seen with more plasticizer present. These findings are consistent with observations reported at the BATT review meeting that the low-temperature ionic conductivity of IM550 is strongly increased by addition of PEG plasticizer. A paper describing these results is in preparation.

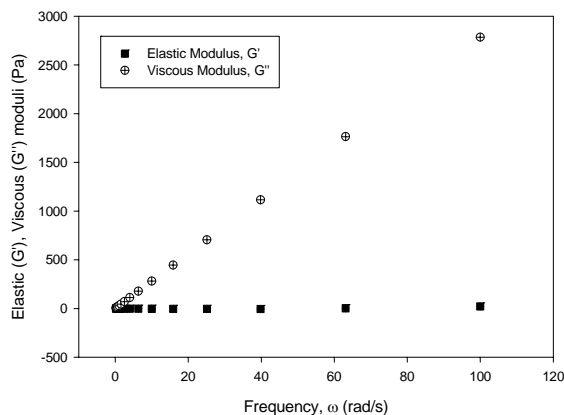


Figure 1. Dynamic rheology data for a sample of IM550 acquired at ambient temperature using a ARES-LS type rheometer from Rheometric Scientific in a cone-and-plate geometry.

Progress was made on two fronts involving measurements. A cell suitable for three-electrode voltammetry experiments inside an inert atmosphere box was fabricated. Experiments will commence when modifications to the box are made to provide electrical connections. Swage-style cells being used for cycle testing are being modified to mitigate problems with water and oxygen in the electrolytes and current collector corrosion. Nickel and Carpenter 20 stainless steel are being used for the anode and cathode current collectors respectively, and cells are being assembled inside an argon-filled glove box to ensure that they are contaminant-free.

In the synthesis area, new ionic melt electrolytes were synthesized having the following structure: PEG-(Imidazolium)⁺(TFSI)⁻-CF₂CFHO-CF₂CF₂SO₂X where X = O(Li) or N(Li)SO₂CF₃ and PEG is monomethyl ether of MW 550 Da. Ionic conductivity and DC polarization studies on these electrolytes are in progress.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith and O. Borodin, University of Utah

TASK TITLE: Electrolytes - Molecular Modeling of Electrolytes and Their Interaction with Electrodes

SYSTEMS: Low-Cost Li-Ion

BARRIERS: Poor cation transport properties of single ion conductor gel electrolytes at ambient temperatures. Poor transport through SEI layer.

OBJECTIVES: Gain molecular level understanding of the cation transport mechanism in liquid electrolytes, single ion conductor gel electrolytes, and ionic liquids. Investigate transport properties of novel gel electrolytes and ionic liquids with improved lithium transference number. Understand lithium transport through the SEI layer and outer SEI layer/electrolyte interface.

APPROACH: Perform virtual synthesis and detailed characterization of a number of single ion conductor electrolytes, ionic liquids and liquid electrolytes using molecular dynamics simulations with developed many-body polarizable force fields. Investigate transport mechanism in electrolytes in details. Based upon learned information about transport mechanism, suggest improved electrolyte chemistries. Perform MD simulations of the SEI layer and SEI/electrolyte interface to predict structural and transport properties in these battery components.

STATUS OCT. 1, 2005: A detailed study of the influence of comb-branched copolymer architecture and EC plasticizer concentration on structural and transport properties of single ion conductor gel electrolytes as a function of temperature will be investigated for the following parameters: the length of side chains and their spacing, salt concentration, and amount of EC plasticizer. The structure and transport properties of the dilithium ethylene dicarbonate model SEI compound will be investigated. Barriers for lithium transport from electrolyte towards model electrolyte-electrode interface will be investigated for liquid electrolytes and dry single ion conductors.

EXPECTED STATUS SEPT. 30, 2006: A number of promising ionic liquids and gel electrolytes based on TFSI⁻ anion anchored to polymer side-chains and oligomers chain ends will be investigated. Various ether-based and carbonate-based polymer and plasticizer couples will be explored in order to minimize electrolyte temperature dependence and improve room temperature conductivity. Barriers for Li⁺ transport near SEI layer and in SEI layer will be studied for gel single ion conductors.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES:

(1) May 2006 – Simulate a number of gel single ion conductors with new plasticizer/polymer couples that have cation transport by vehicular mechanism.

PROGRESS TOWARD MILESTONES

Molecular Dynamics Simulations of Li^+ Transport in SEI Components

During the 4th quarter we have finalized analysis of the MD simulation results for the lithium alkyl monocarbonate (LiMC) and contrasted finding with the previous results for the lithium alkyl dicarbonate SEI components (Li_2EDC). Structure and ion transport in amorphous alkyl carbonates were examined. We found that each Li^+ is coordinated by 4.5-4.7 carboxyl oxygens of EDC^{2-} or MC, with most carbonate groups contributing only one oxygen to the Li^+ first solvation shell. The lifetime of the cages formed by carbonate groups around a Li^+ cation in LiMC was comparable to the residence time of a Li^+ complexation of carbonate groups, while in Li_2EDC these cages lived longer than the residence time of a Li^+ near carbonate groups. This suggests a picture of lithium cations moving along conducting pathways in Li_2EDC is a reasonable first approximation. Conductivity of Li_2EDC extrapolated to $-30\text{ }^\circ\text{C}$ was on the order to 10^{-10} S/cm indicating a significant resistance of this SEI layer component at low temperatures, while conductivity of LiMC was an order of magnitude higher. The Li^+ motion accounted for most of charge transport in Li_2EDC suggesting that Li_2EDC exhibits a single-ion conductor-like behavior. Findings are summarized in Borodin, O.; Smith, G. D. "Molecular Dynamics Simulations of Lithium Alkyl Carbonates" *J. Phys. Chem. B* **2006**, 110 (in press).

MD simulations of SEI components in contact with liquid electrolytes were also studied during 4th quarter.

Molecular Dynamics Simulations of Ionic Liquids

We have revisited the issue of the Li^+ transport mechanisms in ionic liquids (IL) comprised of Li^+ and an anion of bis(trifluoromethanesulfonyl)imide anion (TFSI^-) tethered to oligoethylene oxide (EO) ($\text{EO}_{12}\text{TFSI}/\text{Li}^+$) and contrasted them with the Li^+ transport in a binary solution of the oligoethylene oxide with LiTFSI salt ($\text{EO}_{12}/\text{LiTFSI}$) using molecular dynamics (MD) simulations. It was discerned that structure-diffusion of Li^+ cation in the binary electrolyte ($\text{EO}_{12}/\text{LiTFSI}$) was similar to that in $\text{EO}_{12}\text{TFSI}/\text{Li}^+$ IL at high temperature ($>363\text{ K}$), thus, one can estimate conductivity of IL at this temperature range if one knows the structure-diffusion of Li^+ in the binary electrolyte. However, the rate of structure-diffusion of Li^+ in IL was found to slow more dramatically with decreasing temperature than in the binary electrolyte. Lithium motion together with EO_{12} solvent accounted for 90% of Li^+ transport in $\text{EO}_{12}/\text{LiTFSI}$, while the Li^+ motion together with $\text{EO}_{12}\text{TFSI}^-$ anion contributed approximately half to the total Li^+ transport but did not contribute to the charge transport in IL. Summary of MD simulation results together with experimental findings from the Clemson group lead by Creager and DesMarteau will appear in Borodin, O.; Smith, G. D.; Geiculescu, O.; Creager, S. E.; Hallac, B.; DesMarteau, D. "Li⁺ Transport in Lithium Sulfonylimide-Oligo(ethylene Oxide) Ionic Liquids and Oligo(ethylene oxide) Doped with LiTFSI " *J. Phys. Chem. B*, **2006**, 110, (in press)

In an effort to design ILs with improved Li^+ transport, we have performed additional simulations of the $\text{EO}_{12}\text{TFSI}/\text{Li}^+$ IL that have the Li^+/EO interactions decreased to such degree that 90% of Li^+ are in contact with TFSI^- anions. One can achieve this by fluorination or by introduction of ethylene units, etc. Note, that the original (unmodified) $\text{EO}_{12}\text{TFSI}/\text{Li}^+$ has about 10-20 % of Li^+ in contact with the TFSI^- groups. At 393 K the simulations of the modified IL yield only 20% faster ion transport in comparison with a original $\text{EO}_{12}\text{TFSI}/\text{Li}^+$ IL, however, at 333 K the speed up of ion transport seems larger than 2 times indicating improved low temperature performance for the modified ILs. Additional simulations were initiated to further explore possible improvements of the low temperature behavior of ILs.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Cathode Materials

SYSTEMS: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-voltage, high energy),
Gr/LiBOB+gBL:EA/LiMn₂O₄

BARRIER: Cost and abuse tolerance of Li-ion batteries

OBJECTIVE: To develop low-cost, high-energy and high-power Mn-oxide-based cathodes.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide cathodes for Li-ion cells. Our work will continue to focus on high-voltage, high-capacity electrodes with two-component 'composite' structures, *e.g.*, 'layered-layered' $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ and 'layered-spinel' $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiM}_2\text{O}_4$ electrodes in which M' is predominantly Mn and M is selected predominantly from Mn, Ni and Co. We will evaluate these electrodes in full cells against graphite and intermetallic anodes in conjunction with our anode project (Task 2.1).

STATUS OCT. 1, 2005: Rechargeable capacities greater than 230 mAh/g were achieved from composite 'layered-layered' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes (for $x=0.3$) in lithium half-cells for approximately 50 cycles between 4.8 and 2.75 V at 50 °C when low rates were used (0.25mA/cm²). Composite 'layered-spinel' electrode structures, in which a layered component (Li₂MnO₃) was structurally integrated with a spinel component (Li₄Mn₅O₁₂), were also fabricated, the composition of the spinel component could be modified within the range $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 0.33$) by adjusting the processing temperature. Preliminary data showed that $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{Li}_4\text{M}_5\text{O}_{12}$ 'layered-spinel' electrodes provided a high initial capacity (>250 mAh/g) at low rates but that they did not cycle as well as 'layered-layered' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes.

EXPECTED STATUS SEPT. 30, 2006: Improvements in the electrochemical performance (*i.e.*, capacity, power and cycling stability) of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes and $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiM}_2\text{O}_4$ will have been achieved. Promising electrode compositions will have been evaluated against graphite and metal oxide negative electrodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

MILESTONES: (1) September 2006 - Evaluate compositionally-modified 'layered-layered' $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ and 'layered-spinel' $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiM}_2\text{O}_4$ electrodes with a high Mn content in Li half cells against a technical target of 200 mAh/g for 100 cycles between 4.8 and 2.5 V *vs.* Li⁰ at room temperature and at 50°C. (2) September 2006 - Determine the rate capability and low-temperature behavior of the electrodes and evaluate them in full cells against graphite anodes and the intermetallic anodes of Task 2.1. (3) September 2006 - Probe the interplay between H⁺ and Li⁺ in highly charged and acid-treated electrodes.

PROGRESS TOWARD MILESTONES

Accomplishments

Structurally-integrated ‘layered-layered’ electrodes, represented in two-component notation as $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ ($M=\text{Ni, Mn, Co}$), are under investigation in our group because they provide anomalously high capacities (up to 250 mAh/g or more) in Li cells when cycled between 4.6 and 2.0 V. During the initial charge, Li and oxygen are electrochemically stripped (as Li_2O) from the Li_2MnO_3 component of the electrode structure at ~ 4.6 V (Fig. 1) resulting in an electroactive layered MnO_2 component that remains structurally integrated, but compositionally disordered, with the residual layered $\text{Li}_{1-x}\text{MO}_2$ component. In a collaboration with P. Bruce (St. Andrews University, Scotland) and P. Novák (Paul Scherrer Institute, Switzerland), we have studied the mechanism of this process using combined neutron diffraction (ND) and gas analyses of the system $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ or, in standard layered notation, $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$. Neutron data sets were collected at three points during the initial charge, as shown by the circles in Fig. 1. The total amount of Li extracted at 4.8 V was 1.13 Li per $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ formula unit, 0.4 of which could be compensated for by Ni(II) oxidation (<4.5 V) and 0.73 by oxygen loss (>4.5 V). In-situ differential electrochemical mass spectroscopy (DEMS) demonstrated unequivocally that the 4.6-V plateau observed experimentally was associated with the loss of some oxygen gas. The amount of CO_2 released was estimated to be less than 10% the amount of oxygen. Structural refinements of the electrode during the initial charge to 4.8 V revealed that the small amount of Ni in the Li layer was not significantly mobile; the refinements also confirmed that the removal of Li above 4.5 V was accompanied by the loss of oxygen from the structure. The composition of the electrode at 4.8 V was determined, within experimental error, to be $(\text{Li}_{0.09}\text{Ni}_{0.02})[\text{Mn}_{0.73}\text{Ni}_{0.21}]\text{O}_2$. The structural refinements suggest that as oxygen is evolved from the electrode surface at high potentials, Li vacancies in the transition metal layer become occupied through a cooperative displacement of the transition metal ions from the surface of the electrode structure into the bulk, thereby retaining the close-packed layered character of the structure. Structural models incorporating oxygen deficiencies refined poorly.

A new series of structurally-integrated ‘layered-spinel’ electrodes, $x\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2 \bullet (1-x)\text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ ($0 \leq x \leq 1$), have also been synthesized; they were produced by reacting Li_2CO_3 with appropriate amounts of coprecipitated $\text{Ni}_{1-y}\text{Mn}_y(\text{OH})_z$ precursors at 900°C in air. X-ray diffraction (XRD) patterns provided clear evidence of the coexistence of the layered and spinel components as shown, for example, in the diffraction pattern of $0.6\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2 \bullet 0.4\text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ (Fig. 2). Electrochemical, NMR and TEM data are currently being collected on this series of electrodes; the data will be presented in a future report

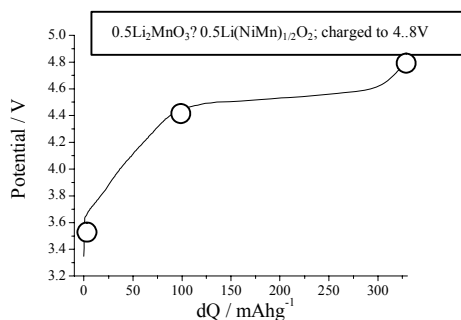


Figure 1. First charge-discharge cycle of (a) as-prepared; (b-d) acid-treated cathodes.

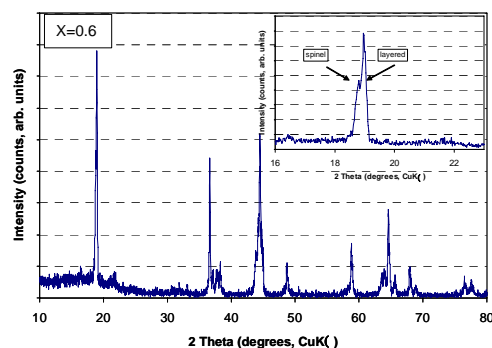


Figure 2. Cycling efficiency of cells (a) as-prepared; (b-d) acid-treated cathodes.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE: Cathodes - Novel Cathodes

SYSTEMS: Li-Ion high-voltage, high energy and low voltage-high stability

BARRIER: Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2005: We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. Addition of other transition metals also prevents structure change at low lithium content to one-block or spinel structures, and changes oxygen evolution behavior. We have completed an electrochemical and thermodynamic evaluation of LiFePO_4 as a base-case low cost cathode, and shown that we can synthesize it hydrothermally at $\leq 200^\circ\text{C}$. We have also studied other iron phosphates, none of which have both a 3.5 V discharge and a capacity exceeding 160 mAh/g.

- LiFePO_4 : > 120 Ah/kg for 100 cycles at 1 mA/cm^2 .
- Layered $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$: 160 and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm^2 respectively.
- Layered $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$ (A = NH_4 or TMA): ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2006: For low-cost Li-Ion cells, we expect to identify the changes in (a) electrochemistry, (b) oxygen evolution (abuse tolerance), (c) high rate capability (HEV), (d) coating effectiveness and (e) the electronic conductivity of LiMnO_2 structures as a function of substitution level as in $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$, so as to determine the optimum minimum substitution level at increased manganese oxide levels. We will also have evaluated the electrochemical behavior of low temperature synthesized iron phosphate as base case cathodes, and explored some higher capacity next generation cathodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

MILESTONES:

- (1) July 2006 – Characterize the electronically stabilized manganese oxide, determine a higher optimum substitution of Mn to obtain a stable high rate abuse tolerant cathode (including application to HEV), and compare the best samples with the base case cathodes.
- (2) July 2006 – Evaluate low temperature iron phosphates and compare them with high temperature LiFePO_4 .

PROGRESS TOWARD MILESTONES

Layered Mixed Metal Oxides. We are continuing our exploration of the effect of reducing cobalt content on the phase $\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$. This quarter we report on the effect of the addition of few per cent excess lithium on the electrochemistry of the phase containing 10% cobalt: $\text{Li}_{1.024}(\text{Ni}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1})_{0.976}\text{O}_2$ where $\text{Li}/\text{TM}=1.05$. The optimum synthesis temperature and its electrochemical properties are listed below:

1. The synthesis temperature was varied from 700 to 1000°C. It was found that the layered character of the structure is almost temperature independent (constant c/a ratio) while the distance between the Li and transition metal layers increases. The temperature was found to have little effect on the Ni disorder; there was around 5% Ni on the Li site. Figure 1(a) shows the increase in crystallinity and particle size as the synthesis temperature is increased.
2. The optimum temperature of synthesis was found to be 800°C giving the largest cycling capacity combined with the smallest polarization. The capacity was found to be 180 mAh/g at 0.5 mA/cm² between voltage limits of 2.5 and 4.6 volts.
3. The 800°C synthesized material held its capacity well over the first 50 cycles. When a lower cycling rate of 0.1 mA/cm² was used, the discharge capacity reached 194 mAh/g.

In Fig. 1(b) the cycling behavior of this Li-rich compound is compared with the Li-stoichiometric material. The former shows an enhanced capacity over the first ten cycles, but then decays to a slightly lower capacity by the fiftieth cycle. There is no clear advantage of the slightly Li-rich sample under the cycling conditions used here of 0.5 mA/cm² between voltage limits of 2.5 and 4.6 volts. In both of these case 5% excess Li was added to the reaction media to obtain the desired composition.

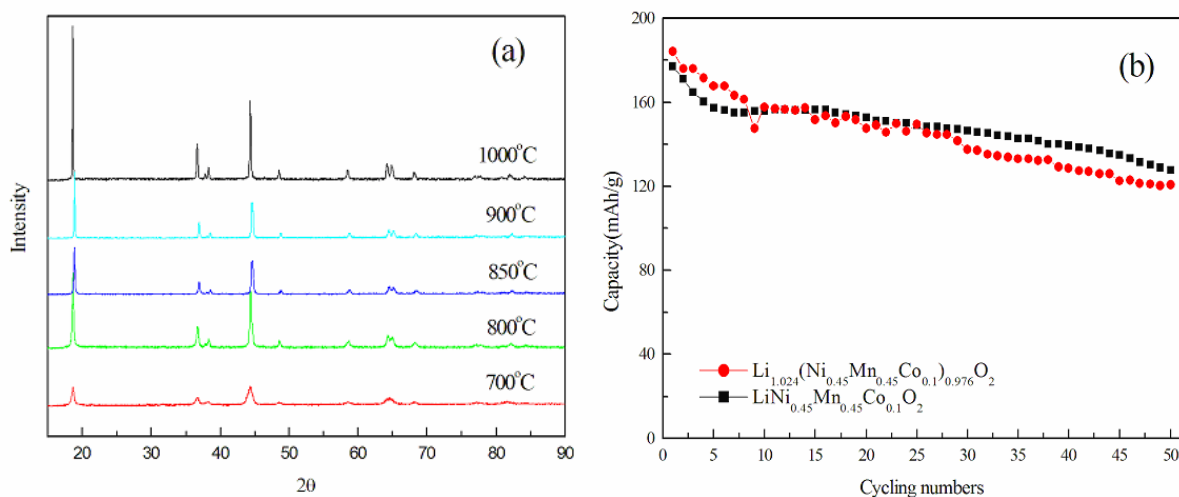


Figure 1. (a) The XRD patterns of $\text{Li}_{1.024}(\text{Ni}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1})_{0.976}\text{O}_2$ prepared at different temperatures and (b) the cycling behavior of $\text{Li}_{1.024}(\text{Ni}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1})_{0.976}\text{O}_2$ compared with $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1}\text{O}_2$.

We are presently investigating increasing the manganese content above that of nickel while maintaining a 10% cobalt level. We are also working with the group of Clare Grey to better understand the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ materials made by ion-exchange from the Na compound.

Publications and Presentations

- (1). J. Chen and M.S. Whittingham, "Hydrothermal Synthesis of Lithium Iron Phosphate," *Electrochem. Commun.*, **8**, 855 (2006).
- (2) M.S. Whittingham, "Overview of New Cathode Material Developments for Lithium Ion Batteries," China Int. Battery Fair, Beijing, China, and Wuhan University, China. July 2006.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Low-voltage, high-stability (LiFePO_4), high-voltage, high energy ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, new manganese oxides), and high voltage, high-power (new manganese oxides)

BARRIERS: Cost, cycle life, abuse-tolerance, energy density, and power density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCAR.

APPROACH: Cathode materials are synthesized by various means. Physical and electrochemical properties (*e.g.*, structure, surface characteristics) are measured in conjunction with members of the diagnostic group. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

STATUS OCT. 1, 2005: Initial screening of novel manganese oxides for manganese dissolution and cycling performance at elevated temperatures has been completed. Tunnel- MnO_2 s are superior to layered materials in terms of abuse-tolerance and are recommended for high power applications. Significant improvement in LiFePO_4 performance was observed when materials were processed with 4-8 wt% pyromellitic acid and 0.5-1 wt% ferrocene (a graphitization catalyst) due to the improved structure of the carbon coating.

EXPECTED STATUS SEPT. 30, 2006: An investigation of the high-voltage capacity of tunnel- MnO_2 s will be carried out to determine if these materials are also suitable for high energy density applications, as well as work directed towards their high-power performance. Work on carbon-coated LiFePO_4 will continue, with emphasis placed on how distribution of carbon affects performance. Some effort will be directed towards co-synthesis of LiFePO_4 with carbon nanotubes. New manganese oxide structures without Ni or Co substituents for high-energy density applications will continue to be surveyed.

RELEVANT USABC GOALS: High power, abuse-tolerance (HEV); High energy density cathode materials that do not contain Ni or Co (EV).

MILESTONES:

- (1) (Sept. 2005-postponed until Dec. 2005) – Recommend the most abuse-tolerant manganese oxide structures for potential HEV applications, and highest energy density manganese oxides containing no Ni or Co for potential high energy applications.
- (2) June 2006 – Determine feasibility (go/no go) of co-synthesizing LiFePO_4 and carbon nanotubes.
- (3) September 2006 – Complete survey of tunnel- MnO_2 structures

PROGRESS TOWARD MILESTONES

4.3a (FY2006)

A TEM examination of the combustion products of ferrocene with or without pyromellitic acid at 700°C shows that carbon nanotubes approximately 5 nm in diameter are produced (Fig. 1). In addition to strong peaks that can be assigned to disordered carbon in the Raman spectra of these products (with R. Kostecki, diagnostics) additional peaks at low wavenumbers that can be assigned to Fe_3C and, possibly, nanotubes are seen. (Fe_3C is an intermediate for nanotube growth). Similar peaks are seen in the Raman spectra of some LiFePO_4 powders processed with ferrocene and pyromellitic acid under similar conditions. Work next quarter will be directed towards correlating the presence of nanotubes (using TEM) with the Raman data so that LiFePO_4 samples can be quickly surveyed. Some work will be directed towards identifying the types of nanotube produced, since helicity and diameter directly affect electronic conductivity.

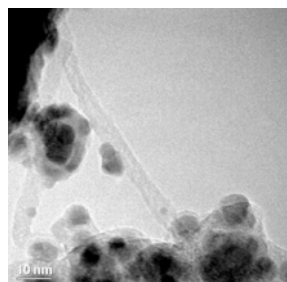
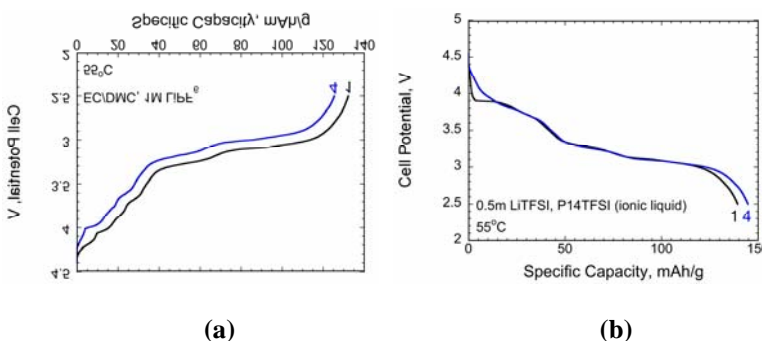


Figure 1. Carbon nanotubes produced by combusting ferrocene at 700°C.



Figures 2a and b: Discharges of $\text{Li}/\text{Li}_x\text{MnO}_2$ cells with LiPF_6 -based electrolyte at 55°C, or ionic liquid electrolyte at 55°C.

4.3b (FY2006)

$\text{Li}/\text{P14TFSI}$, $0.5\text{m LiTFSI}/\text{Li}_x\text{MnO}_2$ or $\text{Li}_x\text{Ti}_{0.11}\text{Mn}_{0.89}\text{O}_2$ cells were built and compared to cells with conventional electrolytes. The room temperature performance of the ionic liquid (P14TFSI) cells is poor, due to the high interfacial impedance at the Li electrode (with J. Kerr, electrolytes), but is improved considerably at 55°C. Advantages to the ionic liquid system include better thermal and oxidative stability and decreased dissolution of manganese oxide electrodes at 55°C compared to LiPF_6 -containing electrolyte systems (see Figs. 2a and b). A new ionic liquid P14FSI has been received from CSIRO in Australia, and is expected to result in better room temperature performance.

Further plans to meet or exceed milestones N/A

Reason for changes from original milestones Milestone 4.3b from FY05 was postponed until Dec. '05 to finish evaluation of storage and cycling tests. It has now been completed.

Publications and Presentations

- (1) "Carbon Surface Layers on a High-Rate LiFePO_4 ," Heike Gabrisch, James D. Wilcox, and Marca M. Doeff, *Electrochem. and Sol. State Lett.*, **9**, A360 (2006).
- (2) "Optimization of Carbon Coatings on LiFePO_4 ," M.M. Doeff, J.D. Wilcox, R. Kostecki, G.Y. Lau, U.S. Patent IB2289P, filed June 13, 2006.

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Li secondary battery

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative *cathode* materials for a lithium-ion battery.

APPROACH: The universal motif of cathodes in rocking chair Li-ion batteries is one of immobilized redox centers that are accessible to electrons from the current collector and Li^+ ions from the electrolyte. Immobilization ensures that the redox units do not transfer to and subsequently poison the anode. Our research is centered around high-power cathodes for the purpose of EVs and HEVs. This translates into pure or composite materials which allow for transfer of electrons *and* Li^+ ion with little or no resistance. We are currently pursuing three different avenues of research: (1) New materials based on conventional oxide structures with proven high rate capabilities, (2) new cathode schemes based on conductive polymers which may serve as a new conductive binder in more conventional composite cathodes, and (3) Substitution into the environmentally benign and cost effective LiFePO_4 to improve rate capabilities.

STATUS OCT. 1, 2005: Substitution of polypyrrole (PPy) for carbon and PTFE binder in LiFePO_4 /PPy composite cathodes was shown to give an increased capacity and rate capability compared to a LiFePO_4 /C/PTFE composite. This innovative approach shows promise of being extendable to other cathode materials.

EXPECTED STATUS Sept. 30, 2006: LiFePO_4 nanoparticles and $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ nanowires will be fabricated and tested in button cells. Analysis of the importance of carbon coating and of crystalline orientation in the nanowires will be under investigation. Fabrication of $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ with PPy will have been explored.

RELEVANT USABC GOALS: 30 ohm-cm^2 area specific impedance, cold cranking capability to -30°C , 300,000 shallow discharge cycles, abuse tolerance to short-circuit and cell overcharge.

MILESTONES:

- (1) February 2006 – Synthesize, test, and evaluate $\text{LiNi}_{2/3}\text{Mn}_{1/3}$ nanowires
- (2) February 2006 – Synthesize, test, and evaluate LiFePO_4 nanoparticles without and with Al substitution for Fe
- (3) September 2006 – Electrochemically characterize the most promising cathode materials fabricated with/without PPy

PROGRESS TOWARD MILESTONES

In our previous work, we tried to develop an alternative carbon-coating technique for LiFePO_4 to be applicable to the C- LiFePO_4 /PPy (PPy: polypyrrole) composite cathodes; we also tried to bond PPy to the layered compound $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$. The results were unsatisfactory. However, we realized that carbon coating, particle size, and the ratio of PPy to the active oxide in the composite are important for both LiFePO_4 and $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$. In the past quarter, we continued the experiment on the LiFePO_4 /PPy and $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ /PPy composite cathodes, and focused on synthesis and surface modification of $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ cathode material.

Oxalic-acid-based coprecipitation was employed to prepare a $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ sample with a high ordered structure. Li^+ , Ni^{2+} and Mn^{2+} acetates were used as starting materials. The effects of stoichiometry in the starting materials and sintering temperature on the structure as well as electrochemical performance were carefully investigated. Rietveld refinement showed that the sample with a 20% excess Li source in the starting materials sintered in air at 600°C for 3 h and further at 900°C for 5 h exhibited a perfect ordered structure. A specific discharge capacity as high as 190 mAh/g was obtained at C/20 in the voltage range of 4.5–2.7 V. As shown in Fig. 1, the ordered $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ sample exhibits an excellent rate capability. Even at 5C, the specific discharge capacity is still higher than 100 mAh/g. However, the cycle stability is not very good. About 24% fade was observed after 50 cycles. In order to enhance cycle life, we coated this sample with carbon, LiAlO_2 , Al_2O_3 and SiO_2 . We found that modification with SiO_2 is more efficient. Figure 2 compares specific capacities vs. cycle number for $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ and SiO_2 (3wt%)-coated $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at a rate of 0.1 C (4.3–2.7V). Only 5% fade in capacity was observed after 100 cycles for the latter. The improvement in cycle stability by SiO_2 modification can be ascribed to the protection of the $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ particles from being dissolved into the electrolyte.

A series of $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($x=0.5, 0.4, 0.33, 0$) samples were prepared with the same coprecipitation method. Analysis by atomic absorption spectrophotometry indicated that the Li^+ content was almost 1.00 for the samples with $x = 0.5, 0.4$ and 0.33 . Rietveld refinement also showed that they all exhibited a well-ordered structure. However, it is difficult for LiNiO_2 to get a stoichiometric composition. Our results indicate that the ordered $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ exhibits the highest capacity among these oxides.

$\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ /PPy composite cathodes were fabricated in different conditions via electrodeposition. However, no improvement in capacity or rate capability was obtained. The ratio of $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ to PPy and the conductivity of the deposited composite film are two main reasons for the poor performance. It is difficult to control the ratio. Furthermore, the conductivity depends on many factors such as doping of PPy and carbon coating of $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$. Carbon coating on $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ particles is more difficult than on LiFePO_4 .

In the next quarter, we will prepare C-coated spherical LiFePO_4 particles from amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ powders synthesized by a controlled crystallization method and then bond the spherical particles to PPy via electrodeposition. Moreover, we will explore some new silicate-based cathode materials.

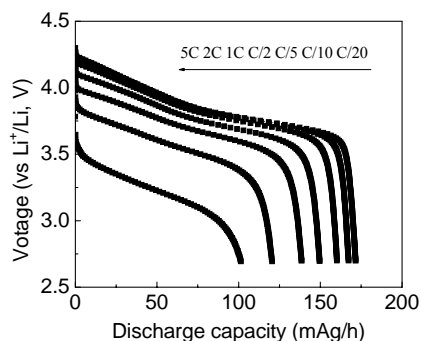


Figure 1. Specific discharge capacity at various rates for the ordered $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ sample (4.3–2.7V).

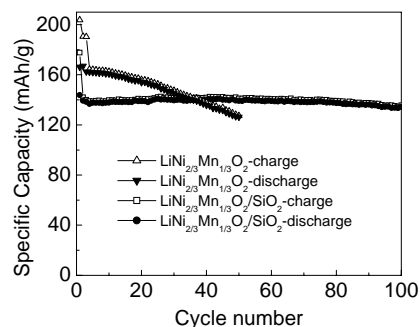


Figure 2. Specific capacity vs. cycle number for the ordered $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ and SiO_2 -coated $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at a rate of 0.1 C (4.3–2.7V).

TASK STATUS REPORT

PI, INSTITUTION: A. Manthiram, University of Texas at Austin

TASK TITLE: Cathodes - Superior Capacity Retention, High Rate Spinel Manganese Oxide Compositions

SYSTEMS: Spinel manganese oxides

BARRIERS: Cycle life, elevated temperature storage, power density, and energy density

OBJECTIVES: To develop low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high rate, low irreversible capacity loss, and good storage characteristics at elevated temperatures.

APPROACH: Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions for manganese, anionic substitutions for oxygen, and an optimization of the microstructure and morphology are being pursued. The spinel oxide compositions are characterized by diffraction, spectroscopic, and electrochemical techniques to establish a structure-composition-property-performance relationship.

STATUS OCT. 1, 2005: Evaluation of the optimized $\text{LiMn}_{2-x-y}\text{Li}_x\text{Ni}_y\text{O}_4$ and $\text{LiMn}_{2-x-y-z}\text{Li}_x\text{M}_y\text{M}'_z\text{O}_4$ (M and M' = transition and non-transition metal ions) spinel oxide compositions (4 V) in Li-ion cells, identification of the factors that control the electrochemical performances of the cation-substituted 5 V spinel oxide system $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, and a comparison of the factors with those of the 4 V spinel oxide cathodes.

EXPECTED STATUS SEPT. 30, 2006: Optimization of the synthesis and processing conditions as well as compositions of the spinel oxyfluoride cathodes, their characterization and electrochemical evaluation, monitoring and comparison of manganese dissolution at different depths of discharge in various spinel cathodes with and without Mn^{3+} and fluorine (4 and 5 V cathodes), comparison and effect of transition metal ion dissolution in spinel, layered, and olivine cathodes.

RELEVANT USABC GOALS: 10-year life, < 20 % capacity fade over a 10-year period

MILESTONES:

- (1) March 2006 – Optimization of the synthesis conditions of oxyfluoride spinels
- (2) September 2006 – Comparison and consequences of metal ion dissolution in various cathodes

PROGRESS TOWARD MILESTONES

In continuation of our optimization of spinel cathodes, we have monitored the manganese dissolution at different depths of discharge (DOD) of the oxyfluoride spinel cathode $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$ and compared the data with those of LiMn_2O_4 . Samples with various DOD were prepared by chemical delithiation with an acetonitrile solution of the oxidizer NO_2BF_4 , and manganese dissolution was measured by soaking the chemically delithiated powders in the electrolyte at 55°C for 7 days. The amount of dissolved Mn from $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($0.14 \leq 1-x \leq 1$) decreases slightly from 3.2 to 2.9 wt% with decreasing Li content due to an increase in the oxidation state of Mn. In contrast, the amount of dissolved Mn from $\text{Li}_{1-x}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$ decreases from 0.8 to 0.6 wt% with decreasing Li content, confirming that the cationic and anionic substitutions help to reduce Mn dissolution and improve the electrochemical performance. However, both the systems exhibit slightly higher Mn dissolution in the two-phase region (3.2 wt% for $\text{Li}_{0.35}\text{Mn}_2\text{O}_4$ and 0.7 wt% for $\text{Li}_{0.37}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$), indicating that the two-phase region may play an important role on Mn dissolution. We have also evaluated the area specific impedance (ASI) of LiMn_2O_4 , $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$, and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$ before and after cycling at 60°C , employing the PNGV L-HPPC test with an 18-s pulse discharge at 5C rate and 2-s pulse charge at 3.75C rate at room temperature. Although all the three samples have a similar ASI value of 25-35 $\Omega\cdot\text{cm}^2$ at 50% DOD before cycling, it increases to 120, 87, and 78 $\Omega\cdot\text{cm}^2$, respectively, for LiMn_2O_4 , $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$, and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$ after cycling at 60°C , possibly due to changes in electrode kinetics, Li-ion diffusion, and ohmic drop. A smaller rise in ASI for the cation-substituted spinel oxide and oxyfluoride attest to their better electrochemical performance compared to LiMn_2O_4 .

In addition to the electrochemical evaluation with Li metal anode, we have now carried out electrochemical tests with Li-ion cells fabricated with the spinel cathodes and commercial carbon or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes at elevated temperatures. While the $\text{LiMn}_2\text{O}_4/\text{C}$ cell shows a severe capacity fade of 33% after 30 cycles with a continuous decline in capacity, the $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4/\text{C}$ and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}/\text{C}$ cells exhibit better cyclability with

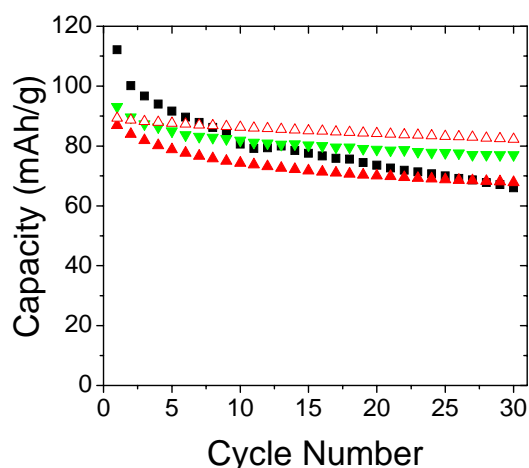


Figure 1. Cyclability of Li-ion cells at 60°C and C/5 rate.

- (■) $\text{LiMn}_2\text{O}_4/\text{C}$
- (▲) $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4/\text{C}$
- (▼) $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}/\text{C}$
- (△) $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$.

a capacity fade of, respectively, 22 and 16% after 30 cycles (Fig. 1). Additionally, with the same $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4$ cathode, the cell fabricated with the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode shows better cyclability than that fabricated with the carbon anode due to the well-known interaction of the dissolved Mn with the carbon anode.

Utilizing the knowledge gained with the 4 V LiMn_2O_4 spinel system, we have also investigated the incorporation of fluorine into the 3 V spinel system $\text{Li}_4\text{Mn}_5\text{O}_{12-\eta}\text{F}_\eta$. While $\text{Li}_4\text{Mn}_5\text{O}_{12}$ synthesized at 600 and 700°C shows a significant amount of the impurity phase Li_2MnO_3 , fluorine incorporation suppresses the impurity phase in $\text{Li}_4\text{Mn}_5\text{O}_{11.9}\text{F}_{0.1}$ (600°C) and $\text{Li}_4\text{Mn}_5\text{O}_{11.83}\text{F}_{0.17}$ (700°C). The fluorine-substituted $\text{Li}_4\text{Mn}_5\text{O}_{11.9}\text{F}_{0.1}$ exhibits a higher initial capacity of 158 mAh/g and a lower capacity fade of 4.3% compared to 151 mAh/g and 6.2% fade for $\text{Li}_4\text{Mn}_5\text{O}_{12}$, due to the suppression of the inactive impurity phase in the former.

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki, LBNL

TASK TITLE: Diagnostics - Electrode Surface Layers

SYSTEMS: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/LiMn₂O₄ (high-voltage, high-power); Gr/LiPF₆+EC:DEC/LiFePO₄ (low-voltage, high-stability)

BARRIER: Short lithium battery calendar/cycle lifetimes.

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface chemistry, morphology, topology, interfacial phenomena, and cell power or capacity decline.

APPROACH: Our approach is to use *in situ* and *ex situ* Raman microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and standard electrochemical techniques to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film or single particle model electrodes. Data to be collected include changes in electrode surface morphology, structure, electronic and ionic conductivity, electrode surface chemistry, SEI thickness and composition, all of which accompany cell cycle-life tests.

STATUS OCT. 1, 2005: We expect to define relationships between electrochemical performance and limitations of BATT baseline systems and cell history, abuse tolerance, electrodes surface properties and interfacial phenomena. We intend to develop good understanding of the key elements for good electrochemical performance of LiFePO₄ and LiMn₂O₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ composite cathodes. We expect to complete the study of the effect of electrode pre-treatment on the evolution of interfacial impedance of electrodes stored in the electrolyte at elevated temperatures. We anticipate completing preliminary experiments to study graphite disordering phenomena in the composite anodes and carbon retreat/rearrangement in the composite cathodes.

EXPECTED STATUS SEPT. 30, 2006: We plan to optimize the microwave plasma-assisted carbon-coating process to obtain electronically conductive and uniform thin films of graphitic carbon directly on LiFePO₄ raw powders. The effect of carbon coating on the cathode electrochemical performance will be evaluated. We expect to develop full understanding of the mechanism of carbon retreat/rearrangement in the composite cathodes and graphite disordering in the carbonaceous composite anodes. We plan to determine their impact on the electrodes' electrochemical performance upon cycling and storage in LiPF₆-EC-EMC electrolytes at ambient conditions and at elevated temperatures. We expect to characterize physico-chemical processes which are responsible for these effects, and establish possible links with other detrimental phenomena.

RELEVANT USABC GOALS: 15 year life, 30 ohm-cm² area-specific impedance, 300,000 shallow discharge cycles.

MILESTONES: June 2006 – Full evaluation of microwave plasma-assisted synthesis of graphitic carbon matrix for composite cathodes.

PROGRESS TOWARD MILESTONES

Our first objective was to optimize the microwave-assisted plasma chemical vapor deposition (MPACVD) of graphitic carbon films and complete the electrochemical evaluation of carbon-coated LiFePO_4 , $\text{LiNi}_{0.8}\text{Co}_{0.14}\text{Al}_{0.06}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite cathodes. Preliminary experiments revealed that the presence of a uniform thin film of conductive graphitic carbon produced by MPACVD directly on LiFePO_4 powders (collaboration with K. Zaghib, Task 1.3 and M. Doeff, Task 4.3) caused improvement of the electrode power performance and cycle life compared to uncoated electrodes. However, electrochemical charge/discharge tests of the composite MPACVD carbon-coated LiFePO_4 cathodes fell short of matching the performance rate of state-of-the-art LiFePO_4 material that was carbon-coated by thermal pyrolysis of organic precursors. We determined that significant differences in the powders' particle size (1-5 μm vs. 200 nm) and morphology were mainly responsible for the observed discrepancies in electrochemical performance of the LiFePO_4 electrodes. In order to make final and coherent conclusions, a new batch of uncoated 200 nm particle size LiFePO_4 powder was procured from Hydro-Québec. The comparative experiments of MPA-coated LiFePO_4 electrodes are still being conducted and a full evaluation of this technology is expected to be completed by the end of September 2006.

We fully evaluated the effect of MPACVD carbon thin-film coating on the electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders. XRD spectra of the microwave carbon-coated cathode materials showed no indication of structural damage or new phase formation due to possible overheating. Low-temperature Ar-plasma, rapid film growth prevented overheating and the consequent reduction of the oxide active material by carbon. Raman spectra of carbon coated powders revealed spectral features typical of the raw materials accompanied by strong D and G bands characteristic of highly graphitized sp^2 -coordinated carbon. A full electrochemical evaluation of carbon-coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite cathodes vs. Li anode in a button cell configuration showed a significant improvement of material utilization, power performance and cycle life of the MPA carbon-coated electrodes vs. uncoated materials (Fig. 1).

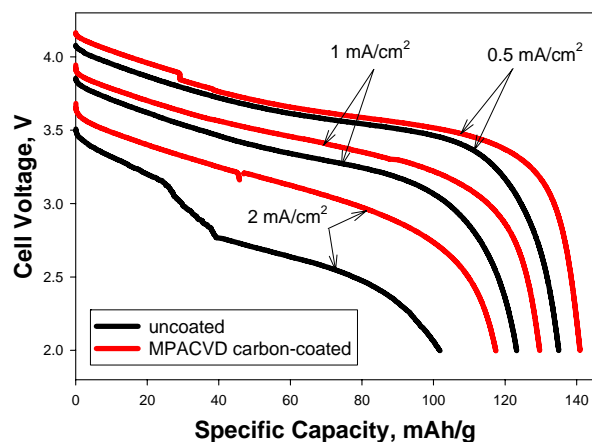


Figure 1. Discharge capacity of (—) uncoated and (—) MPA carbon-coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite electrodes.

We also initiated effort on direct MAPCV synthesis of thin-film carbon-Sn and carbon-Si nano-composite anodes. We determined that interaction of the organo-metallic aromatic precursors with low-pressure Ar-plasma and strong electromagnetic radiation produce highly crystalline graphitic carbon thin-films decorated with metal nano-particles. Preliminary attempts to synthesize graphite-metal nano-composite electrodes from organo-metallic precursors using the MAPCVD method yielded 2-7 μm C-Pt films with Pt nano-particles (<30 nm) uniformly dispersed in the carbon matrix. We will continue to use a similar strategy to synthesize C-Sn and C-Si nano-composite thin films from Sn- and Si-containing organic precursors.

TASK STATUS REPORT

PI, INSTITUTION: W-S. Yoon and X-Q. Yang, Brookhaven National Laboratory

TASK TITLE: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: Gr/LiPF₆+EC:DEC/LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂ (high-voltage, high-energy);
Gr/LiPF₆+EC:DEC/LiFePO₄ (low-voltage, high-energy)

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline.

APPROACH: Our approach is to use a combination of *in situ*, *ex situ* and time resolved synchrotron based x-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish the structural differences between surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. Hard and soft XAS will be used to elucidate the charge compensation mechanisms for cathode materials during electrochemical cycling. *In situ* x-ray diffraction will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at different conditions.

STATUS OCT. 1, 2005: In FY 2005, *in situ* x-ray diffraction (XRD) and a combination of *in situ* and *ex situ* x-ray absorption spectroscopy (XAS) studies of the structurally stabilized LiAl_{0.15}Mn₂O₄ spinel materials cycled at different temperatures have been completed, the studies of the effects of new electrolytes and additives on the stability of LiMn₂O₄ electrodes at elevated temperatures were also completed. Using newly developed time resolved XRD technique, a systematic study of the structural changes of a series of cathode materials during heating with the presence of electrolyte has been completed. The formation of Li₂CO₃ was observed. The implication on the thermal stability of this newly reported observation has been studied and reported.

EXPECTED STATUS SEPT. 30, 2006: We expect to complete the *in situ* XRD work on LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ cathode materials cycled at elevated temperatures. We also expect to complete the *in situ* XRD and XAS studies of LiFePO₄ obtained from different sources during cycling at different charge-discharge rates. Soft X-ray XAS using partial electron yield and fluorescence yield detectors will be applied to various cathode materials at the O, F, and P K edges and at the L₃ and L₂ edges of the 3d transition metals.

RELEVANT USABC GOALS: 15 year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- (1) April 2006 – Complete *in situ* XRD studies of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ cathode material cycled at elevated temperatures
- (2) September 2006 – Complete the *in situ* XRD and XAS studies of LiFePO₄ obtained from different sources during cycling at different charge-discharge rates.

PROGRESS TOWARD MILESTONES

We have continued to investigate the electronic structural changes for the electrochemically delithiated $\text{Li}_{1-x}\text{Fe}_{1-y}\text{M}_y\text{PO}_4$ ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}$) materials using *in situ* metal K-edge XAS and *ex situ* P K-edge XAS. Figure shows normalized P K-edge XANES spectra of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ electrode as a function of x . The white line gradually moves towards higher energy side as Li is extracted. The major charge compensation of $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ during Li extraction is achieved by the oxidation of Fe^{2+} and Co^{2+} ions to Fe^{3+} and Co^{3+} ions resulting in more covalent Fe-O and Co-O bonds. In the olivine LiMPO_4 structure, polarization of the electrons of the oxygen ions towards the phosphorus ion reduces the covalent bonding to the iron ion by the inductive effect. Likewise the increased covalency of M ($=\text{Fe}, \text{Co}$)-O bonds makes P-O bonds less covalent by the same inductive effect. A shift of P K-edge white line to higher energy position could reflect a reduction in degree of covalency of the P-O bond altered by the presence of the more covalent M-O bond during charge.

It is notable that chemical changes beyond the first coordination sphere around the phosphorus atoms have a systematic influence on the observed XANES spectrum. No pre-edge peak was observed in P K-edge XANES spectrum for the pristine $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$. Upon Li deintercalation, however, pre-edge peaks start to appear in the lower energy region of the main edge. The pre-edge features of P K-edge XAS in transition metal phosphates reflects the interaction between metal 3d and P 3p states through the shared oxygen atom. The gradual increase of pre-edge peak intensities with the Li-ion extraction at low states of charge ($x < 0.4$) shows that these pre-edge peaks are mainly due to the hybridization of P 3p states with the Fe 3d states since this is consistent with the gradual increase in oxidation state of Fe ions with the Li-ion extraction. In contrast, at high states of charge ($x > 0.4$) the peak intensity of the pre-edge shows relatively smaller change indicating that Co site is not rigorously involved in the hybridization of P 3p states with the M 3d states. It is important to note that such hybridization between P 3p and M 3d states occurs in spite of the presence of oxygen atoms that separate phosphorus ions from metal ions. Consequently, the electronic structure of orthophosphates cannot be

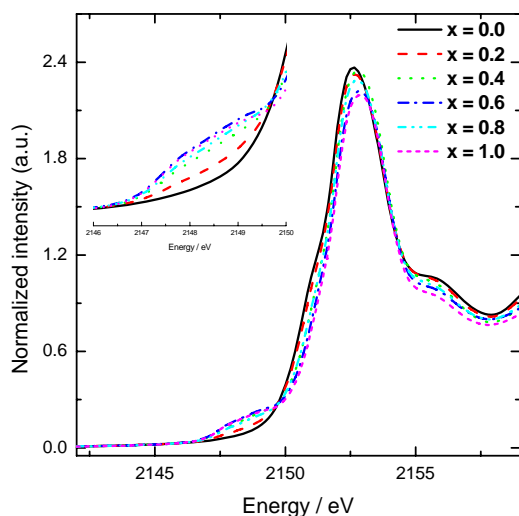


Figure 1. Normalized P K-edge XANES spectra of the $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ electrode as a function of x .

regarded rigorously as composed of traditional ion pairs for $(\text{Li}^+)(\text{M}^{2+})-(\text{PO}_4^{3-})$ and $(\text{M}^{3+})-(\text{PO}_4^{3-})$ which are charged according to their formal valence.

Selected publications

- (1) Won-Sub Yoon, Kyung Yoon Chung, James McBreen, Karim Zaghib, and Xiao-Qing Yang, "Electronic Structure of the Electrochemically Delithiated $\text{Li}_{1-x}\text{FePO}_4$ Electrodes Investigated by P K-edge X-ray Absorption Spectroscopy," *Electrochemical and Solid-State Letters*, **9**, A415 (2006).
- (2) Won-Sub Yoon, Kyung Yoon Chung, James McBreen, and Xiao-Qing Yang, "A Comparative Study on Structural Changes of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ during First Charge Using in situ XRD," *electrochemistry communications*, **8**, 1257 (2006).

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics - Interfacial and Reactivity Studies

SYSTEMS: High Power Battery

BARRIER: Short battery lifetime; Low temperature performance

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use *ex-situ* and *in-situ* Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and ac impedance.

STATUS OCT. 1, 2005: Irreversible changes to graphite anodes due to charging (regen) at low temperature will be determined and correlated to cell chemistry.

EXPECTED STATUS SEPT. 30, 2006: The correlation between impedance rise in graphite anodes at low temperature and composition/structure of the SEI layer determined by FTIR will be established.

RELEVANT USABC GOALS: < 20% capacity fade over a 15-year period.

MILESTONES: September 2006 – Establish correlation between impedance rise in graphite anodes at low temperature and composition/structure of the SEI layer determined by FTIR.

PROGRESS TOWARD MILESTONES: PI has retired; project is suspended.

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology,
C.P. Grey, SUNY Stony Brook

TASK TITLE: Diagnostics - First Principles Calculations and NMR Spectroscopy of Cathode Materials

SYSTEMS: Doped lithium nickel manganese oxides; lithium iron phosphates; layered materials

BARRIERS: Low rate capabilities, high cost, poor stability.

OBJECTIVES: Determine the effect of structure on stability of cathodes. Explore rate limitations and relation to structure.

APPROACH: Use solid state NMR to characterize local and diffraction/TEM for long range structure, as a function of sample preparation method, state of charge, and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, and the effect of structure on cell voltages and identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT. 1, 2005: LiFePO₄ studies by NMR will be ongoing. NMR studies of local structure of Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O₂ following cycling to high voltages will have been completed. Conductivity and transport modeling in LiFePO₄ will be ongoing. Development of methodology to predict stability of electrodes will be started.

EXPECTED STATUS SEPT. 30, 2006: Neutron diffraction studies of charged Li[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O₂ $x = 0.5$ cells will be completed. Results will have been compared with predictions from calculations. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT Program will be ongoing. Stability and conductivity models will have been tested.

RELEVANT USABC GOALS: 10 year life, < 20% capacity fade; 30 ohm/cm² area-specific impedance.

MILESTONES:

- (1) November 2005 – Initiate studies on conductivity in LiFePO₄ (NMR).
- (2) November 2005 – Acquire neutron diffraction data for the charged materials Li_{1-x}[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O₂ and initiate data analysis
- (3) November 2005 – Perform initial tests with methodology for stability prediction.
- (4) May 2006 – Complete analysis of the structure of Li_{1-x}[Li_{(1-2x)/3}Ni_xMn_{2/3-x/3}]O₂ during and after charging (by diffraction) and relate to performance.
- (5) May 2006 – Develop modeling and optimization approaches for rate capability of Ni-Mn based layered materials and LiFePO₄.

PROGRESS TOWARD MILESTONES

We have continued our investigation of stability and rate issues in cathode materials. Using a novel *ab initio* approach we have been able to compute the phase diagram of the $\text{FePO}_4 - \text{LiFePO}_4$ system (Fig 1). In this approach, the Li-vacancy disorder and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ disorder, and their interaction, are fully accounted for. Even though the phase diagram has a highly unusual shape it is in excellent agreement with the experimental work performed by the groups of Masquelier in France and Fultz at Caltech. The system is phase separating between FePO_4 and LiFePO_4 at room temperature, but moderately elevated temperature leads to the formation of a solid solution. Our work shows that this solid solution is driven by electronic disorder rather than by the typical ionic configurational entropy. This is the first system ever in which electronic disorder has been shown to drive solid solution formation and is further confirmation that in this material the Li-vacancy motion is strongly coupled to the electronic structure. We will use the

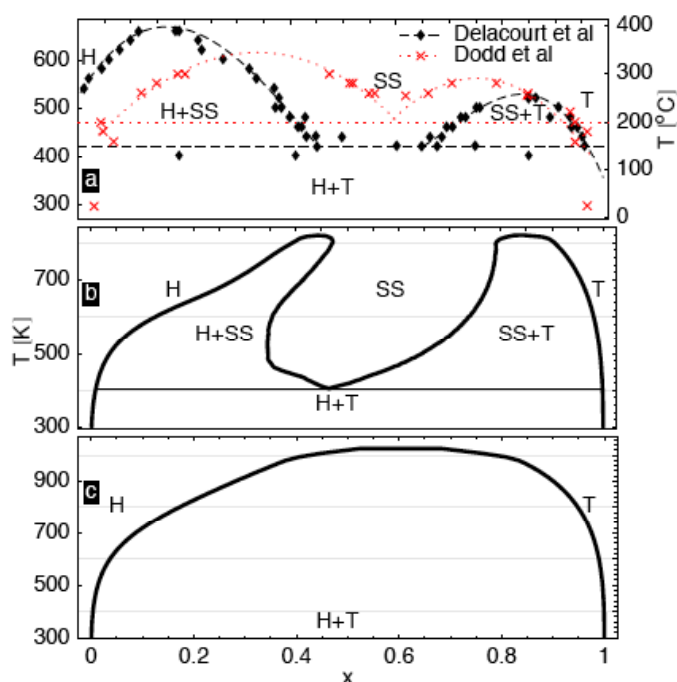


Figure 1. Li_xFePO_4 phase diagram: a) experimental phase boundary data taken from Delacourt *et al* and from Dodd *et al*; b) calculated with both Li and electron degrees of freedom and c) with explicit Li vacancy disorder only.

structural information learned from this study with the previously obtained migration barriers for electrons and Li^+ ions to construct an integrated model for the intrinsic rate capability of LiFePO_4 electrodes. Variable temperature $^{6,7}\text{Li}$ and ^{31}P NMR studies, below and above the phase separation/solid solution transition, are in progress to investigate the timescales of Li-ion mobility. We are continuing our work on the recently developed high rate $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ material. Our current focus is on the ion-exchange process by which $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ is formed from $\text{Na}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ and on the local structure of this material before and after cycling. We have evidence that some structural damage occurs during the ion-exchange process, which is performed at relatively high temperatures and under oxidizing conditions, and are looking for ways to prevent it. We are also continuing the development of methods to predict

the thermal stability of electrode materials at the top of charge through novel LDA+U techniques. We have currently benchmarked the approach on the decomposition of highly charged LiCoO_2 , LiNiO_2 and LiMn_2O_4 . In each case the decomposition temperatures and phases that occur along the decomposition path are in good agreement with experiment. We will report on the results of this investigation in the following report and will soon initiate decomposition predictions for other electrode materials.

TASK STATUS REPORT

PI, INSTITUTION: T.M. Devine, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics - Corrosion of Current Collectors

SYSTEMS: Gr/LiPF₆+EC:DEC/LiFePO₄ and Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

BARRIERS: Inadequate corrosion resistance of aluminum current collectors

OBJECTIVES: Confirm the susceptibility of Al current collectors to underdeposit corrosion (udc), which is a form of crevice corrosion, in LiPF₆ electrolytes by inspecting the current collectors of ~50 additional life-tested coin cells. Determine the mechanism of udc and, in particular, determine the effect of temperature (25 to 60°C) and the influence of cathodes, such as LiFePO₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, in causing udc. Establish the effectiveness of remedial actions, such as modifications to Al surface film and the addition of inhibitors on crevice corrosion resistance. Determine the effect of remedial actions against udc on the battery's discharge capacity and power.

APPROACH: The research proposed for FY2006 consists of five tasks: (1) determine the mechanism of udc of Al current collectors, in particular determine role of cathodes and temperature on udc; (2) evaluate remedial actions, which consist of modifying the Al surface and adding inhibitors to the electrolyte; (3) develop a short-time laboratory test of udc (for mechanistic study and for evaluating remedial actions); (4) assess effects of most effective remedial action(s) on performance of battery; (5) microscopically inspect (for evidence of corrosion) Al current collectors of ~50 additional coin cells previously charge/discharge tested by Marca Doeffer (to bolster earlier conclusions regarding practical importance of corrosion and to confirm that corrosion occurs by udc.).

STATUS OCT. 1, 2005: Short-term udc test will be developed (Task 3). Udc tests of aluminum with different crevice formers will be underway (Task 1). Aluminum electrodes with anodized films formed in sulfuric acid (to produce 1-10nm thin layer of Al₂O₃) and in battery electrolytes (to produce duplex film with outer layers of AlF₃ or AlBO₃) will be prepared and coated with cathodes of LiFePO₄ (Tasks 2 and 4). Inspection of current collectors from life-tested coin cells will continue (Task 5).

EXPECTED STATUS SEPT. 30, 2006: The contribution of corrosion of current collectors to a battery's overall loss of capacity and the improvements due to remedial actions will be quantified. The mechanism of crevice corrosion of Al and the role of cathodes and temperature in causing corrosion of Al current collectors in electrolytes with LiPF₆ will be identified.

RELEVANT USABC GOALS: 10 year life; < 20% capacity fade.

MILESTONES:

- (1) August 2006 – Determine the specific role of cathodes such as LiFePO₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ in causing crevice corrosion of aluminum current collectors in battery electrolytes with salts of LiPF₆.
- (2) August 2006 – Determine the effects of remedial actions against corrosion on a battery's loss of capacity.

PROGRESS TOWARD MILESTONES

During the past year, work was focused on (1) inspecting aluminum current collectors in life-tested ATD batteries for evidence of corrosion, and (2) determining the details of the mechanism of corrosion of Al current collectors in Li-ion batteries.

We have examined 19 ATD batteries from GEN2 series that were previously charge/discharge tested at different temperatures ranging from (approximately) 25-60°C. Microscopic inspection of Al current collectors of the ATD batteries was undertaken to confirm results of earlier laboratory corrosion tests of Al and the results of microscopic inspection of life-tested Li-ion coin cells. Both the laboratory corrosion tests and the inspections of the coin cells' current collectors indicated Al current collectors were susceptible to crevice corrosion.

Our results indicate localized corrosion of the Al current collector in all 19 cells even in ATD cells tested at room temperature (25°C) for a short period of time (4 weeks). The results strongly suggest underdeposit corrosion (udc) of the Al current collectors. Our inspections indicate that there are different types of pits; pits that are most likely caused by mechanical deformation, pits that are most likely caused by corrosion and there are pits that are hybrids. One of the possible causes of the pits present in the tested current collectors besides udc is mechanical damage to the aluminum's surface during the attachment of the cathode. The cathode is attached to the current collector by rolling Al current collector covered by the cathode from both sides. However, a very good correlation of number of pits vs. cycling time and the pit-size distribution vs. cycling time indicate that the number of pits and the sizes of pits increase with cycling time and provide additional evidence that corrosion is a significant cause of pitting as the amount of cycling increases. In addition to corrosion of Al current collectors, microscopic investigation revealed cracking of some regions that had sustained pitting corrosion.

We began working with John Kerr on testing the effect of PF_5 generation on localized corrosion of Al current collectors. Al covered with GEN2 cathode was stored for 10 days in EC:EMC electrolyte (1:1 weight ratio) with 0.5M PF_5 gas generated from LiPF_6 solution using John Kerr's system. A white powder was formed on top of the Al under the cathode, but no signs of corrosion were found. EDS analysis of the white powder showed traces of F and P. The penetration of LiPF_6 salt underneath the cathode may contribute to the mechanism of the udc, and demands further studies.

Preliminary results were generated in collaboration with Dr. Justin Salminen on a new project investigating cathode extraction in different ionic liquids. Metals from cathodes of GEN2, LiFePO_4 , $\text{Li}_{1+x}\text{Mn}_{2-2x}\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ were extracted in ionic liquids that contain mainly BF_4 and TFSI groups. Tens of ppm of the specific metals were found in the solution after immersion in ionic liquids for just 2-5 weeks at 50°C.

TASK STATUS REPORT

PI, INSTITUTION: Y. Shao-Horn, Massachusetts Institute of Technology

TASK TITLE: Diagnostics - Microstructure and Transport Properties of Cathode Materials

SYSTEMS: Graphite/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (High-voltage, high energy),
Graphite/LiBOB+γBL:EA/LiMn₂O₄ (high-power)

BARRIER: High cost, poor cycle life and abuse tolerance of Li-ion batteries

OBJECTIVES: The primary objective is to develop low cost, high-energy, and high-power Mn-oxide-based cathodes.

APPROACH: The microstructure of oxide-electrolyte interface with and without nanoparticle coating and its stability as a function of potential and cycle number is examined *ex situ* and *in situ* by transmission electron microscopy and electrochemical atomic force microscopy. Transport processes and properties in the bulk cathode and at the oxide-electrolyte interface, and their changes as a function of potential and cycle number, are analyzed by galvanostatic testing at different current densities, galvanostatic intermittent titration techniques (GITT), and electrochemical impedance spectroscopy (EIS). The correlation between microstructure and transport properties is essential to the optimization of stable, Mn-based cathode systems and the development of new cathode materials, and the production of safe, durable, cost-effective, high-energy or high-power Li-ion batteries.

STATUS OCT. 1, 2005: This is a new project with a start date of Feb. 1, 2006.

EXPECTED STATUS SEPT. 30, 2006: Establish correlation between the microstructure and transport properties for uncoated LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ and LiMn₂O₄.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

MILESTONE: September 2006 – Complete EIS, GITT and TEM studies of commercially available, layered LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂.

PROGRESS TOWARD MILESTONE

As AlPO_4 nanoparticle coating on LiCoO_2 has been reported to show the best rate and cycling stability to high voltages with respect to other coating chemistry, we here apply $\text{Al}_x\text{P}_y\text{O}_z$ nanoparticles coating onto LiMn_2O_4 samples and examine the cycling stability of LiMn_2O_4 . Aluminum-sec-butoxide was mixed with unhydrous H_3PO_4 in iso-propanol solvent, then sol mixed in ultrasonic bath and dropped on the $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ powder. Solid-liquid mixture was grinded for 30 minutes by ball-milling to enhance the wetting of solid particles, which was then dried at 120°C for 1h and heat-treated at 700°C for 3h with a heating rate of $5^\circ\text{C}/\text{min}$.

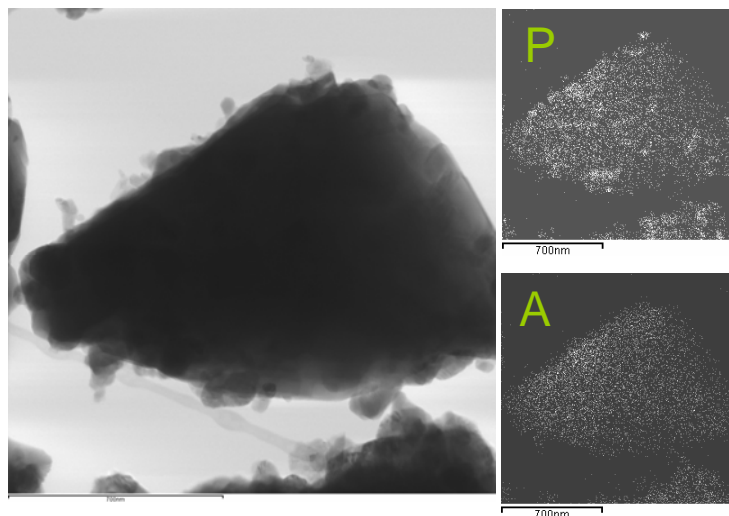


Figure 1. A TEM image of the 2wt% $\text{Al}_x\text{P}_y\text{O}_z$ coated $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ sample (Left); STEM EDX mapping of P and Al on the crystal on the left (Right).

Transmission electron microscopy (TEM) studies showed that these nanoparticles had crystal sizes in the range of 20-50nm and they appear to be crystalline. In addition, it should be noted that the surfaces were not well covered. The exact crystal structures of the nanoparticles are being investigated currently. Scanning transmission electron microscopy and energy dispersive spectroscopy of 2wt% and 5wt% coated samples showed that both P and Al elements were uniformly distributed on the particles. Although the coated samples showed better cycling stability than uncoated samples, preliminary results showed that the coated samples had much lower capacities than the uncoated electrodes

at intermediate current densities such as C/5. Efforts will be focused on understanding the coating microstructure and chemistry, reducing the particle size and improving particle coverage.

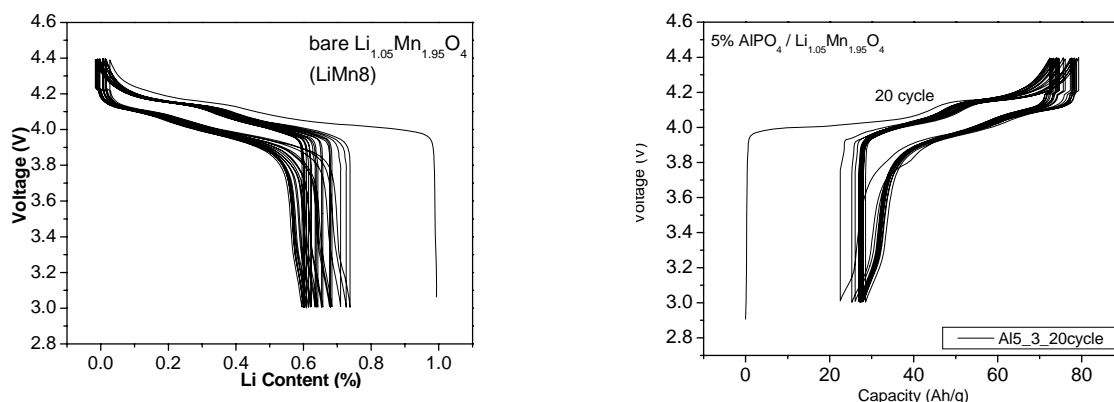


Figure 2. Voltage profiles of $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ -uncoated cycled at a rate of C/5 (Left); Voltage profiles of $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ -5wt%coated cycled at a rate of C/5.

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE: Modeling - Improved Electrochemical Models

SYSTEMS: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-voltage, high-energy); Gr/LiBOB+γBL:EA/LiMn₂O₄ (high-voltage, high-power); Gr/LiPF₆+EC:DEC/LiFePO₄ (low-voltage, high-stability)

BARRIERS: Poor transport properties, capacity, and power fade

OBJECTIVES: Develop experimental methods for measuring transport and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport properties in liquid electrolytes.

STATUS OCT. 1, 2005: Work is completed on a model for calculating stress distributions in electrode materials during intercalation. Full characterization of transport in LiPF₆ electrolytes is ongoing. Optimization of the lithium titanate spinel electrode has begun.

EXPECTED STATUS SEPT. 30, 2006: Optimization of lithium titanate spinel in various systems will be ongoing. Full characterization of transport in LiPF₆ electrolytes will be ongoing. Incorporation of side reactions into dualfoil for lithium-ion cells will begin. A new project will begin, possibly on the distribution of resistance between active materials connected to a current collector.

RELEVANT USABC GOALS: 30 ohm-cm² area-specific impedance, Cold cranking capability to -30°C, 300,000 shallow discharge cycles, Abuse tolerance to cell overcharge and short circuit

MILESTONES: May 2006 – Fully characterize transport in a binary electrolyte.

PROGRESS TOWARD MILESTONES

Transport Property Measurement

A technique for measuring diffusion coefficients in electrolytes for lithium-ion batteries has been developed. This technique is simple, inexpensive, and accurate. Full characterization of transport in a binary electrolyte entails the measurement of the conductivity, diffusion coefficient, and the transference number. The conductivity has been characterized for several electrolytic solutions as a function of concentration. A new technique for measuring the transference number in these electrolytes is under development. This investigation should be complete by December 2006.

The new method for diffusion-coefficient measurement in Li-battery electrolytes avoids the effects of side reactions. This method is a modification of the technique of restricted diffusion and does not require the use of electrodes. The experimental setup now allows for temperature control in acetonitrile as well as the Gen2 electrolyte. Results indicate that the diffusion coefficient for LiPF_6 is a factor of four higher in acetonitrile than in baseline electrolytes. The technique has shown reproducible results that compare well with literature values.

In addition, a modeling effort has begun, investigating the effect of various parameters including particle size and porosity on the high-charge-rate behavior of an asymmetric hybrid supercapacitor system that has been developed by the Energy Storage Group at Rutgers. This technology involves the use of a lithium titanate spinel anode and activated carbon cathode. Work has begun to account for concentration changes in the electrolyte in a system model.

Side reactions in electroactive polymers are currently under investigation as well. An effort is underway to measure the open-circuit potential of poly(3-butylthiophene) accurately as a function of state of charge. This was previously not possible due to self discharge.

Using Flat-Voltage Profile Electrodes to Increase the Capacity Usage of Li-ion Batteries in Hybrid-Electric Vehicles

Work is being continued to determine the effect that flat open-circuit potential profiles have on increasing the capacity usage of batteries. Charge and discharge simulations are being run using a Mn_2O_4 cathode and a carbon anode, and the resulting SOC range for driving cycles is being determined. By comparing this SOC range with that obtained by using an artificial flat open-circuit potential, the hypothetical advantage to using a flat open-circuit potential, which is inherent to the LiFePO_4 and lithium titanate spinel coupling, will be able to be quantified. One particular challenge for plug-in hybrid electric vehicles is that batteries will experience a rigorous duty cycle, involving daily deep discharges far beyond those of today's hybrid electric vehicles. A battery with a flat-voltage profile therefore, will be especially beneficial for this type of application. Other battery issues, such as battery versus engine size, pertinent to PHEVs are also being investigated.

TASK STATUS REPORT

PI, INSTITUTION: V. Srinivasan and J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE: Modeling - Understanding the Behavior of Advanced Li-ion Chemistries Using Mathematical Modeling

SYSTEMS: LiFePO_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and LiMn_2O_4 all vs. graphite

BARRIERS: Poor low-temperature operation, low power capability, capacity/power fade.

OBJECTIVES: Understand and quantify the behavior of the BATT chemistries. Use models to quantify the performance of new electrolytes and cathodes made in the program. Develop methodologies to estimate transport properties in cathodes

APPROACH: Develop mathematical models for various Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to compare various chemistries with each other and assess their ability to meet EV and HEV goals.

STATUS OCT. 1, 2005: The fast charge capability of the LiFePO_4 cathode will be quantified. Experiments that are designed to understand the phase behavior of the LiFePO_4 cathode will be ongoing.

EXPECTED STATUS SEPT. 30, 2006: A comprehensive quantification of the phase behavior of the LiFePO_4 system will be complete. A quantification of the low-temperature behavior of the LiFePO_4 cathode will be complete. Efforts to understand the spinel-L333 mixture materials will be on going. Development of models for the advanced materials synthesized in the BATT Program will be ongoing.

RELEVANT USABC GOALS: $\text{ASI} = 30 \text{ } \Omega\text{-cm}^2$, Cold cranking capability to -30°C , 300,000 shallow discharge cycles

MILESTONES:

- (1) December 2005 – Quantify the impact of the phase behavior of LiFePO_4 cathode during HEV operation
- (2) May 2006 – Complete model for the spinel-layered mixture material.

PROGRESS TOWARD MILESTONES

Milestone 1: Milestone 1 has been completed and the results reported in the first quarterly report for FY 2006.

Milestone 2: Our second milestone relates to the development of a model for the spinel-layered mixture material where the LiMn_2O_4 spinel is physically mixed with a $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode. Interest in this material stems from reports in the literature that suggest that adding the layered material results in a decrease in the rate of manganese dissolution from the spinel cathode. This decrease is expected to result in an increase in the cycle life of spinel-based cells. However, it is far from clear as to why this interesting phenomenon occurs. We therefore attempted to begin studies on this topic by developing a macrohomogeneous model that accounts for the behavior of this mixed cathode. We have previously developed models for each cathode system individually and compared the model to experimental data on well-characterized cells. We have since extending our models to incorporate two different particles. The second particle is allowed to have different thermodynamic, kinetic, and transport properties, thereby allowing us to describe the features of a different material. This framework allows us to describe the behavior of two different materials physically mixed to fabricate a cathode.

Our next step in this study is to collect experimental data on half-cells with Li-reference electrodes. In addition, there is some interest in this material from the Cathode Group with efforts to perform systematic studies on several such combinations in FY 2007. Therefore we anticipate waiting for these studies to reach fruition before using the mathematical model to study this system further.

Other Research: We are continuing on our modeling effort in order to estimate the usefulness of the various Li-ion chemistries for HEV applications. Specifically, we have started analyzing the correlation between the ASI and the maximum power, at a power to energy ratio defined by the DOE goals. The methodology involves using the mathematical model to perform the HPPC pulse test on a battery of specified design (*i.e.*, thickness, porosity, and anode to cathode ratio) and evaluating the ASI as a function of DOD, the subsequently, the discharge and regen power *vs.* DOD. This information is then used to calculate the DOD range of operation and obtain a plot of the maximum power *vs.* the available energy from which the DOD range which satisfies the goal is identified. This procedure is repeated for various values of the pulse current and cell designs. Results suggest that for the spinel-graphite cell, the ASI decreased with increasing pulse current until a pulse of 30 C. This decrease can be attributed to the kinetic resistance in the system. In addition, increasing the thickness of the cathode decreases the ASI until a point where liquid-phase limitations dominate. However, interestingly, the model suggests that the optimum design is not at the minimum ASI value, but at a thickness that is smaller than that value. In other words, choosing a battery design based on a minimum in the ASI does not allow us to capture the maximum performance of the chemistry. This result occurs because as the electrode is made thicker, the ASI does not decrease at the same rate as the increase in the weight of the cell. Consequently, the specific power decreases. The study suggests that care should be taken when comparing different chemistries with each other only based on ASI data.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan, Ann Arbor

TASK TITLE: Modeling - Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

SYSTEMS: Low-cost Li-ion batteries

BARRIERS: Short lithium battery lifetimes

OBJECTIVES: Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the LiFePO_4 cathode. Develop scale-bridging simulations which will allow identification of the best particle morphologies for both energy- and power-dense systems. Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

APPROACH: Using new simulations developed to model conductivity of the particle networks within both anodes and cathodes, we will expand our investigations with three major new thrusts: 1) development of scale-bridging models to determine likely electrochemical performance of cathode materials, taking direct account of the effects of particle shape and connectivity; 2) determination of the effect of mechanical compression on real batteries, accounting for both multiple layers and cell compression, and 3) extensive experimental and numerical simulation of conduction in new materials synthesized by other BATT workers (Battaglia, Zaghbi, Wheeler), and provision of guidance concerning the best morphologies to use.

STATUS OCT. 1, 2005: Experiments (LBNL and UM) and simulations on conduction and electrochemical performance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

EXPECTED STATUS SEPT. 30, 2006: Correlation of cathode performance with particle morphology, including fiber additives will be made. Completion of conductivity and mechanical experiments to quantify losses under realistic loads will be made.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:

- (1) December 2005 – Predict conductivity in electrodes fabricated by Battaglia at LBNL, develop optimized electrodes for minimum resistivity, minimum mass, maximum failure strength.
- (2) January 2006 – Development of coupled electrochemical/mechanical simulations of small arrays within cathodes, with prediction of charge densities in particles.
- (3) June 2006 – Expansion of algorithms to allow prediction of electrochemical performance of available particle shapes and sizes, in collaboration with Battaglia, Srinivasan.
- (4) June 2006 – Experimental verification of conductivity, reactivity of cathode materials *via* AFM.

PROGRESS TOWARD MILESTONES

• Accomplishment toward milestones over last quarter

Modeling—Electrochemical Performance: In this quarter, we have continued to refine our 3D finite element model which couples electrochemical and mechanical performance of electrodes. Experimental results by Macklin *et al.* [1] are being used for validation of the hypothesis of low ionic mobility with heat treatment of host particles. We are now examining the effect of host particle size on cell performance. Next, we will incorporate realistic microstructures of porous electrodes, and determine stresses and strains within single particle and among particles, due to intercalation of Li ions during the charge and discharge.

Electrode Design: We are using mathematical models to identify optimal mixtures of the materials for dry electrodes, in order to achieve high electronic conductivity and capacity. Our prior collision model is being used to generate structures, whereupon a finite element analysis package, ABAQUS/STANDARD, is employed to determine conductivity of the dry electrodes. Analysis of variance (ANOVA) was used to identify ingredients which most affect conductivity. We are investigating four baseline host materials: LiMn_2O_4 , $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, and LiFePO_4 , mixing with the graphite and carbon black as conductive additives, and PvdF as binder. Both homogeneous and shell-core structures have been modeled.

• Reason for changes from original milestone: N/A

Reference:

1. W. J. Macklin, R. J. Neat, and R. J. Powell, Performance of Lithium Manganese Oxide Spinel Electrodes in a Lithium Polymer Electrolyte Cell. *Journal of Power Sources*, **34**, 1, 39-49 (1991).